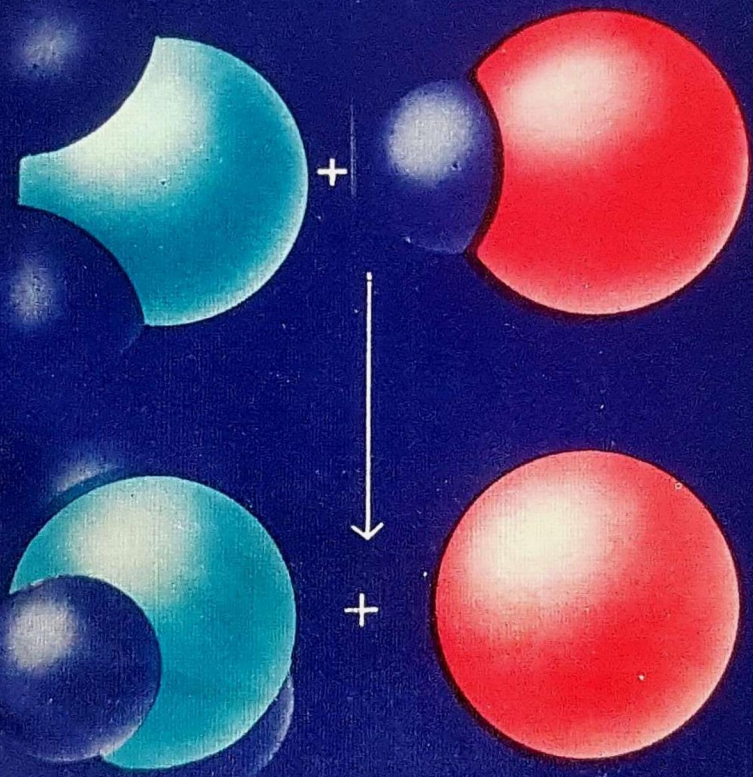
Yu.M.Erokhin and V.I.Frolov

PROBLEMS and EXERCISES in CHEMISTRY



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СБОРНИК ЗАДАЧ И УПРАЖНЕНИЙ ПО ХИМИИ

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PROBLEMS and EXERCISES in CHEMISTRY

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PREFACE

The current *Problems and Exercises in Chemistry* deals with inorganic and organic chemistry. To assimilate the varied facets of chemistry dealing with the physical and chemical principles and descriptive chemistry of both inorganic and organic systems, a chemistry student must be able to solve a large number of problems without any supervision. The present book is meant to develop this ability.

The book consists of eight Chapters, which are further divided into Sections and even subsections. Each Section starts with simple and concise theoretical material followed by illustrative examples. At the end of each Section a lot of problems have been presented without solutions except that answers are provided at the end of the book. These problems are designed to remind a student of previous subjects so that he can see a connection between this and the new knowledge. The "Test Your Knowledge" Chapter is intended to assist the students to reinforce their overall understanding of the factual information gathered in the preceding Chapters.

This collection is mainly for the secondary level of general education. College students and teachers of technical schools may, however, use this book. It may also help students of both professional and academic courses.

1
FUNDAMENTAL CONCEPTS AND LAWS OF INORGANIC CHEMISTRY

1.1 ATOMIC-MOLECULAR THEORY

Atomic-molecular theory is the first theory about the structure of matter. This theory had developed for many centuries on the basis of accumulated experimental data, quantitative notions, mainly physical and chemical ones.

The works of M.V. Lomonosov, the Russian scientist, are of a special importance for the development of the atomic-molecular theory. In the 18th century he predicted very correctly the structure of matter and is, therefore, considered to be the founder of the atomic-molecular theory. The main points of this theory are as follows:

(1) Substances consist of molecules which are physically indivisible particles.

(2) Molecules are in continuous motion.

(3) Molecules are composed of chemically indivisible particles called atoms, which are also in continuous motion.

(4) Atoms have a fixed mass and size.

(5) Molecules of simple substances consist of the same atoms, while those of compounds contain different atoms.

Works of the English physicist and chemist John Dalton have played a great role in the further development of the atomic-molecular theory. Dalton put forward a hypothesis, which states that every chemical element consists of particular atoms. These atoms differ from the atoms of another element. Each substance or chemical compound is made up of molecules which are typical only of a given substance.

The first International Congress of Chemists held in 1860 adopted definitions of the atom and molecule and basic notions of the atomic-molecular theory.

The smallest particle of a substance which possesses a particular mass and retains all the chemical properties of this substance is called a molecule.

In chemical reactions, molecules dissociate to form atoms. An atom, on the contrary, cannot be divided chemically into smaller particles. The atoms may, therefore, be considered as the last stage of chemical dissociation.

Atoms are the smallest chemically indivisible particles that the molecules are composed of.

Atoms and molecules have very small masses. For example, the mass of one of the heaviest atoms, that is, uranium, is 39.54×10^{-23} g, while that of the lightest atoms, i.e., hydrogen is 1.67×10^{-24} g.

It is clear that it is very difficult to use such small numbers in chemical calculations. Therefore it is common practice to use relative masses for the determination of the atomic masses. The *atomic mass unit* (amu), which is $\frac{1}{12}$ of the mass of a carbon atom isotope ^{12}C, has been adopted in physics and chemistry since 1961 as the unit of atomic mass. It is designated by m_a. This unit should be distinguished from the *relative atomic mass* (abbreviated A_r), a dimensionless quantity. For instance, the relative atomic mass of sulphur A_r (S) = 32, while the mass of sulphur atoms m_a (S) = 32 × 1 amu = 32 amu, i.e., equals the relative atomic mass of the element multiplied by 1 atomic mass unit.

The ratio of the mass of a molecule to $\frac{1}{12}$ of the mass of carbon atom is called the *relative molecular mass* of a substance (abbreviated M_r). It equals the sum of relative atomic masses taking into account the number of atoms of each of the elements in the molecule. For example, M_r (H_2SO_4) is made up of

$$2A_r(H) = 2 \times 1 = 2$$
$$1A_r(S) = 1 \times 32 = 32$$
$$4A_r(O) = 4 \times 16 = 64$$
$$M_r(H_2SO_4) = 98$$

The mass of the molecule is calculated accordingly: m_m (H_2SO_4) = 2 × 1 amu + 32 amu + 4 × 16 amu = = 98 amu.

For estimating the quantity of substances participating in chemical reactions, the *molar mass* (*M*) of the substance is used.

The molar mass (M) of a substance is the ratio of its mass to the amount of the substance:

$$M = m/\nu$$

where m is the mass in grams and ν is the amount of the substance in moles. The unit of the molar mass, therefore, is g/mole. The numerical value of the molar mass of a substance coincides with that of the relative molecular mass. For example, the relative molecular mass of a molecule of KOH (a dimensionless quantity), $M_r(KOH) = 56$, the mass of a molecule of KOH (in grams), $m(KOH) = 56$ g, the mass of a molecule of KOH (in amu), $m_m(KOH) = 56$ amu, the molar mass of KOH (in g/mole)

$$M(KOH) = m/\nu = \frac{56\ g}{1\ mole} = 56\ g/mole$$

where ν is the amount of a substance (in mole) containing as many structural units as there are atoms in 12 g of carbon. It has been calculated that 12 g of carbon contain 6×10^{23} atoms. For example, in 1 mole of KOH one can find 6×10^{23} molecules. The number 6×10^{23} has been called the *Avogadro number* in honour of the Italian scientist Amedeo Avogadro. Thus, the mass of a substance and the amount of a substance are different terms.

Example 1. What amount of cupric oxide is contained in 120 g of its mass?

Solution. The relative molecular mass of cupric oxide, $M_r(CuO) = 64 + 16 = 80$. Therefore, the molar mass, $M(CuO) = 80$ g/mole. Now, the amount of the substance can be obtained by using the formula $M = m/\nu$, i.e.,

$$\nu = \frac{m}{M} = \frac{120\ g}{80\ g/mole} = 1.5\ moles$$

Example 2. Determine the mass of 2 moles of sodium hydroxide.

Solution. The molar mass M (NaOH) $= 23 + 16 + 1 =$ $= 40$ g/mole. Therefore, the mass of NaOH, whose amount is 2 moles, is $m = M\nu = 40$ (g/mole) $\times$ 2 moles $= 80$ g.

Example 3. How many atoms are there in 5 moles of phosphorus?

Solution. 1 mole of phosphorus contains 6×10^{23} atoms. Therefore, 5 moles of phosphorus contain $5 \times 6 \times \times 10^{23} = 3 \times 10^{24}$ atoms.

Example 4. How many molecules are there in 80 g of ferric oxide?

Solution. The molar mass of the substance $M(Fe_2O_3) = = 2 \times 56 + 3 \times 16 = 160$ g/mole. Hence, the amount of Fe_2O_3 in 80 g of the oxide can be calculated as follows:

$$\nu = \frac{m}{M} = \frac{80 \text{ g}}{160 \text{ g/mole}} = 0.5 \text{ mole}$$

Taking into account that 1 mole of any substance contains 6×10^{23} structural units, we find the number of molecules in 0.5 mole of ferric oxide as $0.5 \times 6 \times 10^{23} = = 3 \times 10^{23}$.

To calculate the volumes of gases, one uses Avogadro's hypothesis and its corollaries are made use of. The Avogadro's hypothesis is enunciated as follows.

At the same temperature and pressure, equal volumes of all gases contain the same number of molecules.

To determine the volume of gaseous substances, the molar volume V_m is used.

The molar volume of a substance is the ratio of its volume to its amount

$$V_m = V/\nu,$$

where V is the volume in litres and ν is the amount of the substance in moles. At standard temperature and pressure (STP) (i.e. at 273 K and 101.325 kPa), the molar volume of the gases for all gaseous substances equals 22.4 l/mole. If gases occupy one and the same volume, then 1 mole of any gas will contain, at STP, the same number of molecules.

Example 5. Determine the volume of 16 g of SO_2 gas at STP.

Solution. The molar mass, $M(SO_2) = 64$ g/mole, which is 16 g : 64 g/mole = 0.25 mole. Now, 1 mole of SO_2 occupies 22.4 litres at STP, therefore, 0.25 mole will occupy

$$\frac{0.25 \text{ mole} \times 22.4 \text{ litres}}{1 \text{ mole}} = 5.6 \text{ litres}$$

Example 6. Determine the amount of carbon dioxide, which occupies a volume of 5.6 litres at STP.

Solution. The molar mass, $M(CO_2) = 44$ g/mole, which means that 44 g of CO_2 occupy the volume of 22.4 litres at STP. Therefore, 5.6 litres of CO_2 will have the mass of

$$\frac{44 \text{ g} \times 5.6 \text{ litres}}{22.4 \text{ litres}} = 11 \text{ g}$$

Hence, the amount of the substance CO_2:

$$\nu = \frac{m}{M} = \frac{11 \text{ g}}{44 \text{ g/mole}} = 0.25 \text{ mole}$$

or, by employing the molar volume V_m, which is constant for all gaseous substances measured at STP we get

$$\nu = \frac{V}{V_m} = \frac{5.6 \text{ litres}}{22.4 \text{ litres/mole}} = 0.25 \text{ mole}$$

Example 7. The mass of nitrogen having a volume of 1 litre at STP equals 1.25 g. Determine the relative molecular mass of nitrogen.

Solution. On the basis of the corollary from the Avogadro's hypothesis we can find the mass of 22.4 litres of N_2 as follows. Since 1 litre of N_2 has a mass of 1.25 g, therefore 22.4 litres of N_2 will have a mass of

$$\frac{22.4 \text{ litres} \times 1.25 \text{ g}}{1 \text{ litre}} = 28 \text{ g}$$

Now we can find the molar mass of nitrogen:

$$M = \frac{m}{\nu} = \frac{28 \text{ g}}{1 \text{ mole}} = 28 \text{ g/mole}$$

The numerical values of the molar mass (M) and the relative molecular mass (M_r) of the substance coincide. Therefore, $M_r(N_2) = 28$.

The molecular mass of a gas can be calculated from the relative density (D). The relative density is the ratio of the masses of equal volumes of different gases. For example:

$$\frac{m(V_{CO_2})}{m(V_{H_2})} = D_{H_2}$$

The relative density of a gas is a dimensionless quantity. The relative density can be determined on the basis of the Avogadro's hypothesis as the ratio of the masses of equal volumes of different gases to their molar masses (or their relative molecular masses) as follows:

$$\frac{m_1}{m_2} = \frac{M_1}{M_2}$$

where m_1 and m_2 are the masses of definite volumes of the first and second gases, and M_1 and M_2 are the molar masses of the first and second gases. The ratio m_1/m_2 is termed as the density of the first gas with respect to the second one and is designated by the letter D. Hence we get the density of the given gas:

$$D = M_1/M_2$$

Example 8. Calculate the relative density of hydrogen sulphide with respect to ammonia.

Solution. Here $M(H_2S) = 34$ g/mole and $M(NH_3) = 17$ g/mole. Therefore,

$$D_{NH_3} = \frac{34 \text{ g/mole}}{17 \text{ g/mole}} = 2$$

Example 9. The relative density of chlorine with respect to air equals 2.448. Calculate the molar mass of chlorine.

Solution. Since, $M(\text{air}) = 29$ g/mole, and $D_{\text{air}}(Cl)_2 = 2.448$, hence $M(Cl_2) = 29 \text{ g/mole} \times 2.448 \approx 71$ g/mole.

PROBLEMS AND EXERCISES

1. Indicate the fundamental points of the atomic-molecular theory.
2. What is the significance of the atomic-molecular theory for chemistry?
3. What is an atom? What is a molecule?
4. What atoms are the following molecules made up of: (a) water, (b) carbon dioxide, (c) hydrochloric acid?
5. What are the atomic and molecular masses?
6. What are the similarities and differences between the mass of an atom and the relative atomic mass?

7. What is the molar mass of a substance? What unit is employed to express it?

8. Is it possible to relate the "mole" concept to the "Avogadro number"?

9. What is the molar volume and what is the unit used to express it?

10. Give the definition of Avogadro's hypothesis. What conditions of the gaseous state are termed as standard?

11. What relationships can be established for various gases on the basis of the Avogadro's hypothesis?

12. How does the relative molecular mass of a gas relate to its relative density? What is termed as the relative density? How is the density of one gas with respect to the other calculated?

13. How many times is an atom of nitrogen lighter than atoms of silicon, iron, gallium, and krypton, respectively?

14. What is termed as the density of a gas with respect to hydrogen?

15. How many molecules are there in 22.4 m^3 of a gas at STP?

16. How many grams are there in (a) 2 moles of molecular oxygen, (b) 5 moles of molecular hydrogen, and (c) 0.01 mole of molecular nitrogen?

17. How many moles are there in (a) 14 g of nitrogen, (b) 48 g of oxygen, (c) 112 g of iron, and (d) 31 g of phosphorus?

18. Determine the mass of (a) 0.1 mole of NaOH, (b) 2 moles of HCl, and (c) 1 mole of H_2SO_4.

19. What amount of a substance is contained in (a) 4.9 g of $Cu(OH)_2$, (b) 0.2 kg of NaOH, and (c) 0.056 ton of KOH?

20. How many molecules are contained in (a) 5.85 kg of NaCl, (b) 0.8 ton of CuO, and (c) 106 kg of Na_2CO_3?

21. How many moles are present in 100 g of the following substances at STP: (a) oxygen, (b) bromine, (c) chlorine, (d) methane, and (e) ammonia?

22. Determine the molecular mass of a gas, if 5 g of it occupy a volume of 4 litres at STP.

23. Determine the densities of the vapours of the following substances with respect to hydrogen and with respect to air: (a) O_2, (b) N_2, (c) Cl_2, (d) CO (the molecular

masses of hydrogen and air may be taken as 2 and 29, respectively).

24. Determine how many times the following substances are heavier than air: (a) H_2S, (b) CO_2, and (c) HCl.

25. The density of a gas with respect to oxygen equals two. Determine the density of this gas with respect to hydrogen.

26. What is the mass of 1 m^3 of each of the following gases at STP: (a) N_2, (b) He, and (c) SO_2?

27. Calculate the volume occupied at STP by (a) 11 g of CO_2, (b) 4 g of CH_4, (c) 71 g of Cl_2, and (d) 8 g of O_2.

28. Find the molecular mass of a gas, if its density with respect to helium is equal to 20.

29. What is the relative molecular mass of a gas, if the mass of 1 litre of it measured at STP equals (a) 0.0899 g, (b) 1.4289 g, (c) 1.2506 g, and (d) 1.96 g?

30. Calculate the mass of a mixture of gases consisting of 11.2 litres of hydrogen and 8 litres of nitrogen taken at STP.

31. A volume of 1 m^3 of a gaseous mixture contains hydrogen (25% by mass), oxygen (25% by mass), and carbon dioxide (50% by mass). Calculate the mass of this mixture.

32. A gaseous mixture contains hydrogen (35% by volume), carbon monoxide (30% by volume), and oxygen (35% by volume). Determine the mass of 1 litre of this mixture.

33. How many molecules and how many moles of a substance are contained in 1 m^3 of a gas at STP?

34. Determine the masses (a) of an atom of potassium, (b) of a bromine, water, and a potassium chloride molecule.

35. What are the masses of (a) 2 moles of atomic oxygen, (b) 3 moles of atomic hydrogen, and (c) 0.01 mole of atomic chlorine?

36. How many atoms of oxygen are there in (a) 32 g of oxygen, (b) 66 g of carbon dioxide, and (c) 64 g of sulphur dioxide?

37. How many molecules are there in 1 litre of any gas at STP?

38. What volume do 10^{24} molecules of (a) oxygen, (b) nitrogen, (c) chlorine occupy at STP?

39. The density of chlorine vapour with respect to air equals 2.44. Determine the composition of chlorine molecules.

40. Compare the number of atoms in 10 g of chlorine with that in 10 g of nitrogen. In which case and how many times is the number of atoms larger?

41. A molecule of a substance has a mass of $16.27 \times \times 10^{-23}$ g. Determine the molar mass of the substance.

42. Calculate how many times the molar mass of nitric acid is greater than that of ammonia.

43. Calculate the mass of 1/4 mole of nitrogen.

44. How many moles of sodium chloride are contained in 234 g of the substance?

45. What is the mass of 0.2 mole of orthophosphoric acid?

46. Determine the relative molecular mass of a gas, if it is known that 1 litre of this gas has a mass of 1.25 g, while 1 litre of air weighs 1.29 g.

47. What volume will be occupied by 9.6 g of sulphur dioxide at STP?

48. Calculate how many times the mass of a nitrogen atom is higher or lower than the mass of chlorine, oxygen, and neon atoms, respectively.

49. Decide where more molecules are present: (a) in 5 g of sulphur dioxide or 3 g of carbon dioxide, (b) in 4 g of hydrogen or 2 g of nitrogen, (c) in 1.6 g of oxygen or 3.2 g of sulphur dioxide.

50. Determine the number of moles of cupric sulphate needed for the preparation of 196 g of cupric hydroxide.

51. How many atoms of aluminium are there in 1 mole of aluminium sulphate?

52. Calculate the mass of a sample of metallic sodium containing as many atoms of sodium as 30 g of aluminium contain.

53. Use the atomic masses of chemical elements expressed in g to calculate the values of atomic masses in amu:

(a) $m_a(\mathrm{K}) = 6.5 \times 10^{-23}$ g, $m_a(\mathrm{Cu}) = 10.6 \times 10^{-23}$ g

(b) $m_a(\mathrm{O}) = 2.6 \times 10^{-23}$ g, $m_a(\mathrm{P}) = 5.15 \times 10^{-23}$ g

(c) $m_a(\mathrm{Ca}) = 6.6 \times 10^{-23}$ g, $m_a(\mathrm{Si}) = 4.7 \times 10^{-23}$ g

54. What is the amount of a substance containing (a) 12×10^{23} molecules, (b) 3×10^{21} molecules, and (c) 6×10^{25} molecules?

55. How many particles are there in 1 mole of a substance?

1.2 THE LAWS OF CHEMICAL COMBINATION

The law of definite composition. While studying the composition of various substances, the French scientist J.L. Proust came to the conclusion that the mass ratios of elements in compounds are always constant, irrespective of their preparation methods.

This means that atoms of elements combine only in definite quantitative proportions to form compounds. To illustrate, common salt may be prepared by different methods, but it always consists of sodium and chlorine. Moreover, the mass ratio of these two elements will always remain constant, i.e., 23 : 35.5. Thus, on the basis of experiments the *law of definite proportions* was put forward (J.L. Proust, 1799) which states that

"in all well known compounds, the proportions of the elements are in certain definite ratios to each other."

Calculations from chemical formulas. If one knows the formula of a substance and the atomic masses of elements, one can carry out various calculations from chemical formulas.

1. *Calculation of mass-percent of an element in a compound.*

Example 1. Calculate the mass percent of copper in CuO.

Solution. $M_r(CuO) = 64 + 16 = 80$, i.e. a mole of CuO has a mass of 80 g and contains 64 g of Cu. Therefore, mass percent of copper in CuO is

$$\frac{64 \text{ g} \times 100\%}{80 \text{ g}} = 80\%$$

2. *Calculation of composition of a compound in mass percents from its chemical formula.*

Example 2. Calculate the composition of cupric sulphate ($CuSO_4$) in mass percents.

Solution. The molar mass $M(CuSO_4) = 160$ g/mole. For calculation let us take a sample of 1 mole of copper sulphate. Then we can write

$$m(CuSO_4) = M\nu = (160 \text{ g/mole}) \times (1 \text{ mole}) = 160 \text{ g}$$

Now, if we assume $m(CuSO_4) = 160$ g as 100%, then

$$\text{mass percent of copper} = \frac{64 \text{ g} \times 100\%}{160 \text{ g}} = 40\%$$

$$\text{mass percent of sulphur} = \frac{32 \text{ g} \times 100\%}{160 \text{ g}} = 20\%$$

$$\text{mass percent of oxygen} = \frac{64 \text{ g} \times 100\%}{160 \text{ g}} = 40\%$$

3. *Calculation of atomic mass of an element from the known mass of a compound.*

Example 3. Calculate how many grams of copper can be found in 40 g of CuO.

Solution. $M(CuO) = 80$ g/mole, $m(CuO) = 80$ g. It means that 80 g of CuO contain 64 g of copper. Therefore, in 40 g of CuO one can find

$$\frac{40 \text{ g} \times 64 \text{ g}}{80 \text{ g}} = 32 \text{ g of copper}$$

4. *Calculation of empirical formula of a substance from its known composition (in mass percents).*

Example 4. Calculate the empirical (simplest) formula of a substance which contains (by mass) 63.64% of nitrogen and 36.36% of oxygen.

Solution. Let X be the number of nitrogen atoms and Y be the number of oxygen atoms in the compound. Since the mass of a nitrogen atom equals 14 amu and that of oxygen atom 16 amu, the mass of all nitrogen atoms and all oxygen atoms in one molecule will be $14X$ and $16Y$, respectively. Now the ratio of the last two masses gives the composition for the whole substance. But this very composition is expressed by the ratio 63.64 : 36.36. Equalizing both ratios, we get the following proportion:

$$14X : 16Y = 63.64 : 36.36 \text{ or}$$

$$X : Y = \frac{63.64}{14} : \frac{36.36}{16} = 4.54 : 2.27$$

To express the ratio $X : Y$ in terms of whole numbers, we divide both members of the right-hand ratio by the smallest of the two. As a result, we get $X : Y = \frac{4.54}{2.27} : \frac{2.27}{2.27} = 2 : 1$. Thus, $X = 2$ and $Y = 1$. This means that in one molecule of the given substance there is one atom of oxygen for every two nitrogen atoms. Hence, the empirical formula is N_2O.

The law of equivalents or reciprocals proportion. Before the creation of the atomic-molecular theory, it was established that elements and compounds take part in chemical reactions in definite mass proportions. This resulted in the discovery at the end of the 18th century of the *law of equivalents* or *reciprocal proportions* according to which

"the weight of an atom of an element is the same in all its compounds, so that the composition of a compound of two elements A and C may be deduced from the compositions of compounds of each with a third element B."

One should distinguish between chemical equivalents of elements and compounds.

The equivalent of an element is such an amount of a substance in moles which either combines with one mole of hydrogen atoms, or substitutes in compounds the same number of hydrogen atoms.

To determine the equivalent of an element, one should know the ratio between the masses of this element and any other element with which the former combines to form a compound and whose equivalent is known. The law of equivalents may be mathematically expressed as follows:

$$\frac{m_1}{\mathrm{Eq}_1} = \frac{m_2}{\mathrm{Eq}_2}$$

The mass of one equivalent of a substance expressed in grams per mole is termed as the equivalent mass of this substance.

The chemical equivalent is not a fixed quantity. It depends upon the valence of the element present in one or the other compound. For example, in SO_2, sulphur is tetravalent, so its equivalent mass will equal 64 (g/mo-

le)/4 = 16 g/mole. Likewise, the equivalent mass of SO_3 = 80 (g/mole)/6 = 13.3 g/mole, the valence of sulphur here being 6. The equivalent of oxygen is equal to 8, since the valence of oxygen is always equal to two: $Eq_{O_2} = 16/2 = 8$. Some more examples are given below.

Example 5. Determine the equivalent of a metal, if it is known that its oxide contains 60% by mass of oxygen.

Solution. It follows from the conditions specified that 40 parts by mass of the metal combine with 60 parts by mass of oxygen to form the oxide. Now, the equivalent of oxygen equals 8. So, according to the law of equivalents, we can calculate the equivalent of the metal (Eq_M) as follows:

$$Eq_M = \frac{m_M Eq_{O_2}}{m_{O_2}} = \frac{40 \times 8}{60} = 5.3$$

Example 6. A metal whose equivalent equals 12 liberates from an acid 0.56 litre of hydrogen gas measured at STP. Calculate the mass of the metal.

Solution. According to the law of equivalents $m_M : Eq_M = m_{H_2} : Eq_{H_2}$. If one of the substances is in the gaseous state, then for calculating the equivalent one can substitute in the above expression for the law of equivalents the mass units for the volume units. Therefore,

$$\frac{m_{H_2}}{Eq_{H_2}} = \frac{V_{H_2}}{V_{Eq_{H_2}}}$$

where V_{H_2} is the volume of hydrogen in cm^3 and $V_{Eq_{H_2}}$ the volume of one equivalent of hydrogen in cm^3.

Then we get the following relationship:

$$\frac{m_M}{Eq_M} = \frac{V_{H_2}}{V_{Eq_{H_2}}}$$

from which $V_{Eq_{H_2}} = 22.4$ litres/2 = 11.2 litres.

Now substituting the values from the conditions specified, we get the mass of the metal:

$$m_M = \frac{12 \text{ g} \times 0.56 \text{ litre}}{11.2 \text{ litres}} = 0.6 \text{ g}$$

The atomic and equivalent masses, and valence of an element are related by the following relationship:

$$\mathrm{Eq} = \frac{A}{n}$$

where Eq, A and n are the equivalent mass, atomic mass and valence of the element, respectively.

Example 7. 8 g of a bivalent metal when treated with an acid liberates 4.48 litres of hydrogen, measured at STP. Calculate the atomic mass of the metal.

Solution. Equivalent mass of the metal is equal to

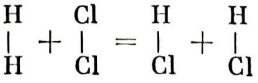
$$\mathrm{Eq_M} = \frac{m_\mathrm{M} V_{\mathrm{Eq_{H_2}}}}{V_{\mathrm{H_2}}} = \frac{8\ \mathrm{g} \times 11.2\ \mathrm{litres}}{4.48\ \mathrm{litres}} = 20\ \mathrm{g}$$

Therefore, the atomic mass of the metal, $A = \mathrm{Eq} \times n = (20 \times 2)\ \mathrm{g} = 40\ \mathrm{g}$.

Law of conservation of mass. The law of conservation of mass of a substance which was discovered by the Russian scientist M.V. Lomonosov in 1748 is stated nowadays as follows:

In every chemical reaction, the masses before and after the reaction are the same.

From the viewpoint of atomic-molecular theory the law of conservation of mass is explained by the fact that during chemical reactions atoms neither get lost (disappear) nor appear from nothing. The total number of atoms before and after a reaction remains the same. Since atoms have a constant mass, this leads to conservation of mass of a substance after the reaction. In chemical reactions, only recombination (rearrangement) of atoms, i.e. their transition from one substance to another, takes place. For example,



Thus, as a result of chemical reactions, substances change, one set of molecules is transformed into another one, but the number of atoms and their total mass do not change.

PROBLEMS AND EXERCISES

1. State the law of definite composition.
2. By whom and when was the law of conservation of mass formulated?
3. How are the law of definite composition and law of conservation of mass utilized practically?
4. What does a chemical formula represent?
5. What does a chemical equation express?
6. Define the concept of "equivalent".
7. Define what the equivalent of an element is.
8. Write down the mathematical expression for the law of equivalents: (a) for solid substances and (b) for solid and gaseous substances.
9. Calculate the mass percent of oxygen in the following compounds: (a) HNO_3, (b) Ag_2O, (c) KOH, and (d) $Ca_3(PO_4)_2$.
10. Determine the mass percent of nitrogen in: NH_4OH, NH_4NO_3, and N_2O.
11. Find out the composition of the following compounds in mass percents: NaOH, CO_2, $KHCO_3$, $FeOHSO_4$ and $H_4P_2O_7$.
12. What amount of Na_2SO_4 will contain (a) 23 g of sodium? (b) 96 g of sulphur? and (c) 128 g of oxygen?
13. How many grams of oxygen are there in 120 g of (a) MgO, (b) NaOH and (c) $FeSO_4$?
14. How many grams of iron are present in 5 moles of (a) Fe_2O_3, (b) $Fe(OH)_2$ and (c) $FeSO_4$?
15. An ore has the following composition: 80 mass percent of Fe_2O_3, 10 mass percent of FeS_2, and 10 mass percent of FeAsS. What quantity of iron is there in 100 kg of the ore?
16. Calculate the mass of phosphorus in (a) apatite, $Ca_3(PO_4)_2$, having a mass of 1 ton and containing 10% by mass of an impurity, (b) 100 g of superphosphate containing 95% $Ca(H_2PO_4)_2$, and (c) 5 tons of the precipitate ore containing 98% $CaHPO_4 \cdot 2H_2O$.
17. An ore contains 70% CoAsS. What is the mass of Co in 1 ton of the ore?
18. What amount of aluminium sulphate, $Al_2(SO_4)_3$, will contain (a) 108 g of aluminium, (b) 288 g of sulphur, and (c) 96 g of oxygen?

19. Find out the simplest formula of a substance containing 43.2, 11.3, and 45.5% by mass of Na, C, and O, respectively.

20. Derive the formula for a crystal hydrate which contains 9.8, 13, 26, and 51.2% by mass of Mg, S, O, and H_2O, respectively.

21. Find out the simplest formula for sodium hyposulphite, given that it has the following composition (by mass): sodium (29.1%), sulphur (40.5%), and oxygen (30.4%).

22. Calculate the formula of a mineral containing ZnO (73% by mass) and SiO_2 (27% by mass).

23. Calculate the equivalent of sulphur in a compound containing (by mass): 5.92% H and 94.08% S.

24. When 5 g of sulphur are burnt, 10 g of sulphur dioxide, SO_2, are formed. Calculate the equivalent of sulphur.

25. An oxide of an element contains 39.7% by mass of oxygen. Calculate the equivalent of the element.

26. A metal with a mass of 6 g liberates from an acid 0.5 g of hydrogen at STP. Determine the equivalent of the metal.

27. Find out the equivalents of metals in $AgNO_3$, K_2SO_4, $FeCl_3$, PbO, and $NaHCO_3$.

28. 3.6 g of a metal reacts with chlorine to form 14.1 g of a salt. Determine the equivalent of the metal, taking the equivalent of chlorine as 35.

29. Calculate the valence of gold in a compound containing (by mass): 64.9% Au and 35.1% Cl.

30. Determine the valence of carbon in a compound which contains (by mass) : 42.85% carbon and 57.15% oxygen.

31. How many equivalents are there in (a) 60 g of Mg, (b) 230 g of Na, and (c) 108 g of Al?

32. A metal with a mass of 4 g requires 2.24 litres of oxygen, measured at STP, for complete combustion. Calculate the equivalent of this metal.

33. 0.54 g of oxygen combines with 2 g of a tetravalent metal. Guess the metal.

34. On burning, 11.2 g of a trivalent metal liberates 16 g of oxide. Which metal was burnt?

35. The mass of 1 litre of hydrogen is equal to 0.09 g.

How many litres of hydrogen are consumed when a mass of 5 g of calcium is burnt in it?

36. 20 g of a metal are dissolved in hydrochloric acid. How many grams of hydrogen will be liberated, if the equivalent of the metal is (a) 20, (b) 12, (c) 23, and (d) 9?

37. The equivalent of a tetravalent element is 3. What is the mass percent of oxygen in its highest oxide?

38. Name the element which forms a gaseous compound with hydrogen, the mass percent of hydrogen in the compound being 2.47%.

39. When 2.25 g of an alkaline-earth metal is oxidized, 6.25 g of an oxide is formed. Name the metal.

40. The oxide of a metal contains 17.2% by mass of oxygen. The compound formed by this metal with iodine has 6.51% by mass of iodine. Determine the equivalent of iodine.

41. Calculate the valence of chromium in an oxide which contains 68.42% by mass of chromium and 31.58% of oxygen.

42. How many grams of aluminium oxide are formed on oxidation of (a) 0.54 g of aluminium, (b) 4 moles of aluminium?

43. How many grams of oxygen are required for complete combustion (up to CO_2 and H_2O) of the following substances having a mass of 10 g each: (a) methane, CH_4, (b) ethylene, C_2H_4, (c) acetylene, C_2H_2?

44. Which volume of air at STP is required for burning 4 g of sulphur into SO_2 (air may be assumed to contain $\frac{1}{5}$ of oxygen by volume)?

45. How many grams of sodium hydroxide are required for converting 16 g of cupric sulphate into cupric hydroxide?

46. How many litres of oxygen measured at STP are consumed when 9 g of aluminium are burnt?

47. How many grams of sodium chloride are obtained by treating 6 g of sodium hydroxide with 59 g of hydrochloric acid?

48. How many tons of water will react with 20 tons of lime which contains 80% by mass of calcium oxide?

49. How many litres of CO_2 are formed when 4 g of carbon react with 11.2 litres of oxygen measured at STP?

Which of the two elements and in what amount will remain unreacted?

50. How many litres of hydrogen will be liberated at STP, when 2.8 g of iron reacts with sulphuric acid?

51. How many litres of CO_2 measured at STP should be passed into a solution of $Ca(OH)_2$ to precipitate (a) 0.5 mole of calcium carbonate, $CaCO_3$, (b) 200 g of $CaCO_3$, and (c) 1 ton of $CaCO_3$?

52. How many litres of CO_2 measured at STP may be obtained by burning 5 tons of coal which contains 95% by mass of carbon?

53. 15 g of zinc were dissolved in sulphuric acid to yield 4.5 litres of hydrogen at STP. Determine the mass percent of impurities present in zinc.

54. How many litres of CO are formed in a gas generator from 1 kg of coke containing 90% by mass of carbon? What volume of oxygen is required for this purpose?

55. Write down the true formulas for various substances having the same simplest formula and containing 85.7% by mass of C and 14.3% of H. The densities of these substances with respect to air are equal to 1.45, 1.93, 1.89, and 3.38, respectively.

56. Derive the true formula of a substance containing hydrogen, carbon, and oxygen in a mass ratio of 1 : 6 : 4 and having a density of 22 with respect to hydrogen.

57. Deduce the true formula of a substance which contains (by mass) 80% carbon and 20% hydrogen. One litre of this gaseous substance measured at STP has a mass of 1.34 g.

58. Calculate the mass percent of metal in the following compounds: (a) Fe_2O_3, (b) $2Fe_2O_3 \cdot 3H_2O$, (c) Fe_3O_4, (d) $FeCO_3$.

59. Calculate the equivalent of lead, if its mass percent in its oxides is (a) 92.87%, and (b) 86.61%.

60. Calculate the equivalents of the metal in compounds, given that the mass percent of chlorine in them is (a) 14.80%, and (b) 34.26%.

61. Determine the equivalent of iron in its oxide, if seven parts of iron (by mass) combine with two parts of oxygen.

62. When 10 g of zinc are dissolved in an acid, 3.43

litres of hydrogen measured at STP are evolved. Determine the equivalent of zinc.

63. How many moles of aluminium oxide are formed when 51 g of aluminium are burnt in oxygen?

64. How many moles of zinc oxide will be formed when zinc is burnt in 5.6 litres of oxygen measured at STP?

65. 4 g of magnesium oxide were allowed to react with 10 g of sulphuric acid. Which of the two substances and in what amount (in g) will remain unreacted?

66. Combustion of a 6-kg coal sample yielded 10.6 litres of carbon dioxide at STP. Determine the mass percent of carbon in the sample.

1.3 PERIODIC LAW AND MENDELEEV'S PERIODIC TABLE

Scientific discoveries may be characterized by two distinct phases. The first phase includes the establishment of special cases, while during the second phase the discovery itself is made and its implications are understood.

D.I. Mendeleev wrote in this connection that there is not even a single, general law of nature which could be found at once and its approval is always preceded by many presentiments. Mendeleev's predecessors proposed their own classification of the known elements. But all these element arrangements were just like an episode in the research activities. Chemists tried to find a suitable arrangement for the elements. However, none of them studied the interrelations between the elements and their compounds so deeply and thoroughly as D.I. Mendeleev did at the beginning of 1869 when the periodic law was discovered. This law states that

the properties of simple bodies, as well as the forms and properties of compounds of the elements, are periodic functions of the atomic weights of the elements.*

But it was not only the atomic mass that was used by Mendeleev as the basis. None of his contemporaries considered the chemical properties of elements and their relations in the way he did. How can it otherwise be explained that in the periodic table potassium comes

* We remind our reader that the term "atomic weight" was used before the term "relative atomic mass" was introduced.

after argon, nickel follows cobalt, and iodine tellurium, though the former element in each pair has lower atomic weight than the latter one. This appears to contradict the periodic law.

Thus, the periodic table compiled by Mendeleev is based not only on the atomic mass, but on the chemical properties of elements as well. He himself reported his first table (on May 1, 1869) under the title: "Systematization of a set of elements based on their atomic weights and chemical similarities".

Modern investigations have proved that the arrangement of elements in the periodic table by Mendeleev was very correct.

Let us consider, say, the properties of elements placed in a horizontal row in the order of increasing atomic masses:

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic number	11	12	13	14	15	16	17	18
Atomic mass	23	24	27	28	31	32	35.5	40

The monovalent alkali metal, sodium, reacts vigorously with water to yield an alkali:

$$2Na + 2H_2O = 2NaOH + H_2$$

Water reacts well with Na_2O oxide.

On boiling, divalent magnesium reacts slowly with water:

$$Mg + 2H_2O = Mg(OH)_2 + H_2$$

Magnesium hydroxide has a very low solubility in water and has basic properties. Magnesium oxide, MgO, is a basic oxide.

Trivalent aluminium is practically stable with respect to water. It can react with water only when the oxide film has been removed from its surface. The reaction proceeds as follows:

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2$$

Both aluminium hydroxide and aluminium oxide (Al_2O_3) are amphoteric. Metal hydroxides are called bases, whereas nonmetal ones—acids.

The tetravalent nonmetal, silicon, forms an acid, H_2SiO_3, which is weaker than carbonic acid. With hydro-

gen and oxygen this nonmetal forms SiH_4 and SiO_2, respectively.

The pentavalent nonmetal, phosphorus, forms a moderately weak acid, H_3PO_4. With hydrogen and oxygen the corresponding compounds are PH_3 and P_2O_5, respectively.

The hexavalent nonmetal, sulphur, which exhibits distinct nonmetallic properties, forms a strong acid, H_2SO_4. This nonmetal combines with hydrogen and oxygen to yield H_2S and SO_3, respectively.

A very active nonmetal with a valence of seven, chlorine, forms a strong acid, $HClO_4$. The compounds this element forms with hydrogen and oxygen are HCl and Cl_2O_7, respectively.

The last element in this row is argon, Ar, which is an inert gas and does not form compounds.

The properties in the next "octave" (Li, Be, B, C, N, O, F, Ne), as well as in all others change in the same order. Thus, the following regularities are established with an increase in the atomic mass:

1. The metallic properties weaken, while the nonmetallic ones become more pronounced:

NaOH strong base	$Mg(OH)_2$ weak base	$Al(OH)_3 \rightleftharpoons H_3AlO_3$ amphoteric hydroxide	
$H_2SiO_3(H_4SiO_4)$ weak acid	H_3PO_4 moderately weak acid	H_2SO_4 strong acid	$HClO_4$ very strong acid

2. The valence with respect to oxygen (oxygen valence) increases, whereas that with respect to hydrogen (hydrogen valence) decreases:

	I	II	III	IV	V	VI	VII
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
				IV	III	II	I
				H_4Si	H_3P	H_2S	HCl
Summary oxygen and hydrogen valence				8	8	8	8

On gradual transition from one element to another, the chemical properties change by way of negation of negation. Inside a period the metallic properties decrease, while the nonmetallic properties increase.

Each period ends with an inert element which is also a negation of the preceding element. But this repetition occurs on another, higher basis.

In the periodic table one can see how quantitative changes (atomic mass) lead to qualitative changes (chemical properties) and, after arriving at a certain point, an insignificant change in quantity leads to a sharp change in quality, i.e. to jump, e.g., from F to Ne, or from Ne to Na.

Mendeleev expressed the periodic law in the form of the periodic table. There are several versions of the periodic table. The most popular versions in the USSR are the short- and long-period tables. In both forms, the periods are arranged along a horizontal axis, while the Groups along a vertical axis.

A period is a horizontal row of elements in which properties vary from typical metals to typical nonmetals and end with an "inert" gas (with the exception of period 7).

There are seven periods in all. Periods 1, 2 and 3 are termed as short periods, while periods 4, 5, 6, and 7 are referred to as long periods. The first period consists of two elements, the second and third periods contain eight elements each, the fourth and fifth eighteen each. The sixth period contains 32 elements and the seventh one is incomplete.

To make the periodic table concise and easier to handle, 14 elements from period 6, which are similar in chemical properties to lanthanum, have been shifted into a separate row called the lanthanide series. Likewise, elements following actinium have also been arranged in a separate row called the actinide series. Unlike the lanthanides, the actinides differ in their chemical properties (a valence of 3 is typical for the lanthanides, whereas actinides possess variable valence; only elements following Cm do have a valence of 3).

A Group is a vertical column of elements in which the metallic properties increase while going down the column. The modern periodic table contains a total of eight Groups. Each of these is divided into main and secondary subgroups represented by the letters A and B, respectively.

The main subgroups consist of two elements of the short

periods and all other elements situated under these two. For instance, the main subgroup of Group VII, i.e. Group VIIA, is made up of F_2, Cl_2 (gases), Br_2 (a liquid), and I_2 (a solid crystalline substance with metallic lustre).

The secondary subgroups contain only elements of the long periods. All these elements are metals and exhibit similar properties.

PROBLEMS AND EXERCISES

1. In which year was the periodic law discovered? How was it formulated by D.I. Mendeleev?
2. What do you know about the predecessors of D.I. Mendeleev?
3. In Mendeleev's periodic table argon has been placed in front of potassium, cobalt has been placed in front of nickel, while tellurium has been placed before iodine, though the atomic masses of the second elements in the pairs are lower than those of the first ones. Explain why.
4. How is periodicity reflected in the periodic law? What are the main features of this law?
5. Explain the terms period, Group, subgroup as applied to a periodic table.
6. How many periods and how many Groups are there in the periodic table?
7. Which subgroups are called main and which ones secondary?
8. Name the elements present in the main subgroup of Group II (i.e. Group IIA) and in the secondary subgroup of Group I (i.e. Group IB).
9. How do the metallic properties of elements change within a Group and within a period?
10. How do the properties of elements vary as the atomic number rises?
11. Which Groups in the periodic table contain elements that can form gaseous compounds with hydrogen? Which of these compounds have acidic properties?
12. Find in the periodic table the most active metal and the most active nonmetal. Which part of the periodic table is occupied by elements with nonmetallic properties?

13. If in the periodic table boron and astatine are joined by a straight line, then what kind of properties will exhibit the elements falling on the left side of this line?

14. State whether trivalent thallium oxide possesses amphoteric properties or not, if it is known that trivalent aluminium and gallium oxides are amphoteric in nature.

15. Four test tubes with concentrated hydrochloric acid are taken. Then sodium, magnesium, aluminium and silicon are introduced each into the first, second, third and fourth test tubes, respectively. Arrange the metals in the order of their ability to replace hydrogen. How will silicon behave towards the acid?

16. Bromine water is added into sodium chloride and sodium iodide solutions taken in two separate test tubes. In which of the two test tubes will a reaction be observed? Draw a conclusion about the activity in the halogen series.

17. Determine the period, row and Group in which the elements with atomic numbers 14, 24, 52, 63, 76 and 101 are located.

18. What chemical properties should the element with atomic number 34 exhibit? Which element in the periodic table should it resemble most? Explain your answer.

19. An element of the secondary subgroup has a higher oxide, XO_3. Does this element form a gaseous compound with hydrogen? Explain your answer.

20. Which of the two elements of Group VII, chlorine or iodine, exhibits stronger nonmetallic properties? Why? Of these two elements which one forms a stronger acid? Write down the formulas of these acids with a view to the maximum oxygen valences for these elements.

21. Which element of Group I, potassium or cesium has the stronger metallic properties? Why? Which of them forms a stronger hydroxide? How can this hydroxide be prepared?

22. With the help of Mendeleev's periodic table, write down the formulas for the higher oxides of the following elements: manganese, vanadium and germanium.

23. Name the elements on the basis of the following data: (a) the element in question belongs to the fourth period, forms a higher oxide, X_2O_7, and yields a gaseous

compound HX with hydrogen; (b) the element belongs to the fifth period, forms a higher oxide, XO_2, and does not form any gaseous substance with hydrogen; (c) the concerned element is from the fourth period, its higher oxide is XO, and it reacts with hydrogen to afford a salt-like compound, XH_2.

24. Find out the element in the periodic table, which belongs to the fourth period, Group V and exhibits a valence of 6 in its oxide. What is its hydrogen valence?

25. Write down at least three formulas for hydroxides, four formulas for acids and five formulas for salts which would consist of only elements of the third period.

26. Write down the formulas of the higher oxides and their hydroxides for elements with atomic numbers 4, 33, 37, 52, 75 and 81.

27. Making use of Mendeleev's periodic table, write down the formulas of chromic, permanganic and selenic acids.

28. Consulting Mendeleev's periodic table, write down the formulas of strontium oxide, hydroxide, and nitrate.

29. Calculate the mass percents of the following elements in their higher oxides: (a) selenium, (b) rhenium, (c) osmium, and (d) indium.

30. Which hydroxide is a stronger base: $Ca(OH)_2$ or $Ba(OH)_2$, NaOH or KOH? Which acid is stronger: H_2SO_4 or H_2TeO_4, H_3AsO_4 or H_3PO_4? Justify your answers.

31. Write down the formulas of barium periodate, magnesium vanadate, aluminium tellurate, zinc germanate and gallium permanganate.

32. Write down the equations for the reactions between (a) selenic acid and strontium hydroxide, (b) perchloric acid and lithium carbonate, (c) gallium hydroxide and chromic acid.

33. The higher salt-forming oxide of an element has a formula of XO_3. This element forms with hydrogen a gaseous compound which contains 1.54% by mass of hydrogen. Name the element.

34. One of the elements predicted by D.I. Mendeleev belongs to Group III and forms an oxide which contains 25.5 mass percent of oxygen. Name this element.

35. The higher oxide of an element has the formula XO_3. The element forms with hydrogen a compound in

which the mass percent of hydrogen is 5.882. Name the element.

36. 4 g of a bivalent metal react with water to liberate 0.224 litre of hydrogen measured at STP. Name this metal.

37. Which of the two oxides in each set below is more acidic: (a) FeO or Fe_2O_3, (b) Mn_2O_3 or MnO_3?

38. Determine the nature of the oxides of (a) manganese: MnO, Mn_2O_3, MnO_2, MnO_3, Mn_2O_7; (b) chromium: CrO, Cr_2O_3, CrO_3; (c) nitrogen: N_2O, NO, N_2O_3, NO_2, N_2O_5 and (d) phosphorus: P_2O_3, P_2O_5.

39. From the formulas of higher compounds below, determine the Group in which the element Z is situated: (a) ZO_2, HZ, Z_2O_7; (b) Z_2O_5, ZH_3, ZCl_4.

40. Determine the relative atomic mass of an element belonging to Group VI, the higher oxide of which contains 60% by mass of oxygen.

41. Determine the relative atomic mass of an element belonging to Group V. Its hydride contains 8.82% by mass of hydrogen.

42. The chloride of an element belonging to Group III consists of 79.77% by mass of chlorine. Determine the relative atomic mass of the element.

43. The sulphide of a trivalent element contains 64% by mass of sulphur. Calculate the relative atomic mass of the element.

44. The nitride of an element of Group II contains 28% by mass of nitrogen. Determine the relative atomic mass of the element.

45. The carbide of an element belonging to Group II contains 37.5 mass percent of carbon. Determine the relative atomic mass of the element.

46. An element combines with hydrogen to yield a gaseous compound. Its higher oxide has a relative molecular mass of 108 and contains 74 mass percent of oxygen. Which Group and subgroup does the element belong to?

47. When dissolved in water, 1 mole of atoms of an element belonging to Group II forms 171 g of a hydroxide. Guess the element.

48. When dissolved in water, 7.8 g of a metal evolved 2.24 litres of hydrogen measured at STP. Determine the atomic number of the metal.

49. Determine in each of the following cases the atom-

ic number of the element belonging to: (a) period 4, row 4 and Group III; (b) period 6, row 8, Group V; (c) period 3, Group IV; (d) period 5, row 6, Group II.

1.4 THE STRUCTURE OF ATOMS. RADIOACTIVITY. ISOTOPES

In the 19th century most of the scientists acknowledged the existence of atoms. Their notion of atoms was, however, incorrect (metaphysical). An atom was then regarded as the tiniest particle of a substance, as a hard, impenetrable ball that was indivisible under any conditions. Only a few outstanding scientists did believe that the atom has a complicated structure and can be divided under certain conditions.

Discoveries made at the end of the 19th century showed that the structure of atoms is complicated and, under certain conditions, it is possible to convert one atom to another. On the basis of these discoveries, the atomic theory of matter started to develop fast, and the atom was really found to be a complicated system. Particles that were detected first in an atom were electrons.

It has long been known that when heated to a high temperature or exposed to ultraviolet rays, the surface of a metal emits negatively charged particles, as a result of which the metal itself becomes positively charged. The Russian scientist A.G. Stoletov and the English scientist William Crookes carried out experiments which helped clarify this phenomenon.

In 1879 W. Crookes studied the deviation of electron rays in a magnetic or an electric field and the rotation of a ventilator, placed inside a cathode-ray tube, under the influence of high-voltage electric current. The property of the cathode rays to set a body in motion and to deviate in magnetic and electric fields led to the conclusion that these rays are material particles carrying the lowest negative charge. Later, these particles were termed as electrons. The fact that the electrons may be obtained from any electrode irrespective of its material, proves that electrons are the constituent parts of atoms of any element.

In the year of 1896, A.C. Becquerel discovered that uranium compounds are capable of emitting invisible rays which can affect a photographic plate wrapped in a black paper. In continuation of Becquerel's work, M. Sklodovskaya-Curie and P. Curie discovered in 1898 two new elements in a uranium ore, radium and polonium, capable of emitting very active radiations. The Curies established that other elements lying in the seventh period of Mendeleev's periodic table, such as thorium and actinium, also exhibit the same property.

Spontaneous decay of the atoms of elements accompanied by emission of radiation is termed as radioactivity (from Latin "radius", meaning ray and "actius", active).

α rays deviate in the direction of the negative pole and consist of a beam of positively charged α particles. The mass of an α particle is 4 atomic mass units and its initial velocity is about 20,000 km/sec.

β rays bend in the direction of the positive pole and consist of a beam of negatively charged particles called electrons. Their speed varies within the range of 100,000-300,000 km/sec.

γ rays remain undeflected in an electric field. These rays resemble the light rays, but differ from the latter in wavelength which is very short. These rays have a great power to penetrate into various substances which are impenetrable for the ordinary light rays.

M. Sklodovskaya-Curie and other scientists established that when radium undergoes radioactive decay, helium and radon are formed. The latter element was unknown at that time, its mass number being 222. The new discoveries thus proved that an atom is a complicated system and consists of simpler particles.

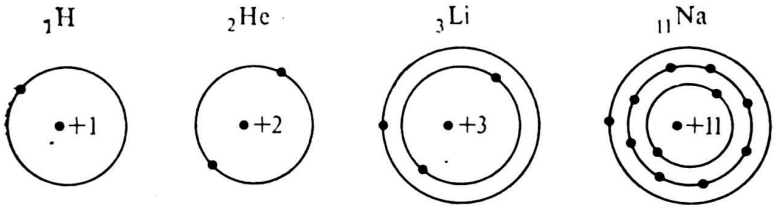
Electrons are emitted from various substances, and thus they are the constituent part of all elements. But electrons are negatively charged particles, while an atom is electrically neutral. This means that in an atom there should be a positively charged part to balance the negatively charged electrons.

While studying the movement of α particles in gases and other substances, the English scientist E. Rutherford together with his students obtained experimental data that confirmed the presence and position of a positively

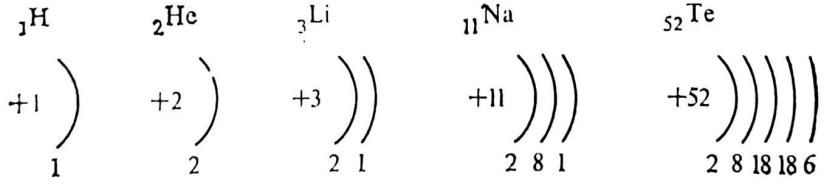
charged nucleus in an atom. In 1911, on the basis of experimental work, Rutherford put forward a hypothesis according to which an atom is a planetary system consisting of a very small nucleus (10^{-12} to 10^{-13} cm) around which electrons revolve in various circular orbits, the number of electrons being as much as to balance the positive charge of the nucleus. The nuclear theory of atomic structure proposed by E. Rutherford got a wide publicity. Later, scientists, however, met with a lot of basic difficulties. For instance, according to notions of classical electrodynamics, an electron, being a charged body, should emit energy in the form of radiation and revolve not in a circle, but rather in a helical curve and finally fall into the nucleus.

Rutherford's theory was, therefore, discarded and replaced by the theory of Niels Bohr. On the basis of the quantum theory of radiation devised by Max Planck, Bohr developed in 1913 the quantum theory of the structure of atoms and constructed a theoretical model of the simplest atom, the hydrogen atom. The following postulates form the basis of Bohr's theory:

1. An electron can revolve around the nucleus of an atom not in arbitrary orbits but only in quite definite, allowed orbits. Bohr's model of atoms is of the following type:



If the orbit is denoted by an arch and the number of electrons by figures, the atomic scheme proposed by Kossel may be represented as follows:



2. While the electron is revolving in these allowed orbits, the respective atom emits no radiation. Energy is given off in the form of radiation or is absorbed, when the electron jumps from one orbit to another. The energy is emitted in the form of discrete portions called quanta. Each of these quanta corresponds to a definite frequency.

A definite amount of energy corresponds to each stationary electronic orbit. When an electron revolves in the first orbit, it is held by the nucleus with a maximum strength, while the energy store of an atom is minimum. Such a state of atom is termed as the *ground state.*

If energy is supplied to an atom, the electron will move to a higher orbit as a result of which the strength of its binding with the nucleus will decrease and the atom's energy store will increase. This is an *excited state* of the atom. Any atom exists only one millionth of a second in the excited state after which the respective electron returns to its initial orbit. Electron transition from a higher orbit to a lower one is accompanied by the emission of a quantum of radiation energy.

To characterize an orbit, Bohr introduced quantum number which was later termed as the *principal quantum number* and denoted by the letter n. The number of orbits for an element is determined by the period number. Since there are seven periods in all, so there exist energy shells 1, 2, 3, 4, 5, 6 and 7 which are also termed as quantum shells and designated by capital letters K, L, M, N, O, P, and Q, respectively. The total number of electrons in a quantum shell or energy level may be calculated from the formula $N = 2n^2$, where n represents the shell number.

For elements in the main or A subgroups, the number of electrons in the last or outermost quantum shell equals the Group number. For elements belonging to the secondary or B subgroups, the number of electrons in the last quantum shell is equal to 2. A few exceptions are Cu, Ag, Au, Nb, Mo, Cr, Ru, Rh, Pt (each containing 1 electron in the last shell), Pd (with no electron in the last shell).

Bohr's theory was developed by the German physicist A. Sommerfeld (1915-1916). He supposed elliptical orbits for atoms, in addition to circular orbits. Therefore, one

quantum number was insufficient to characterize the movement of electron in an atom. So, Sommerfeld introduced the second quantum number called the *orbital quantum number*. The atomic theory developed by N. Bohr and A. Sommerfeld was, no doubt, a big success, but, as a whole, proved to be a failure. Bohr and Sommerfeld based their atomic theory on the assumption that one can determine both the position and velocity of an electron simultaneously and monitor its movement in an orbit. Both these assumptions proved to be incorrect. Then the German physicist Werner Heisenberg deduced in 1927 the uncertainty principle. It states that for small particles in motion like an electron, it is impossible to simultaneously determine its position and velocity at any given instant to an arbitrary degree of precision.

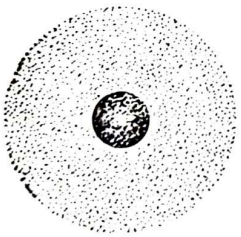
Two basic postulates formed the basis of this new quantum-mechanical approach to the structure of atoms. These are as follows:

1. An electron may be considered as a particle which, while in motion, exhibits wave properties.

2. An electron may be found at any distance from the nucleus. But the probability of its finding at different points in the atom is different.

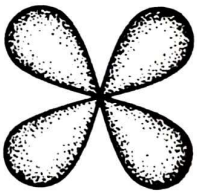
With the development of wave mechanics, the previous notions of the fixed orbits were refused. Bohr and Sommerfeld in their atomic theory considered orbits as lines, whereas quantum mechanics introduced the concept of orbit in space, i.e. an orbital, which is seen as a definite combination of electron positions in an atom.

An electron may be at any point in the space around the nucleus. Therefore, quantum mechanics uses the concept of electron cloud. Electron cloud (orbital in other words) has different geometrical shapes:



1*s*

2*p*



3*d*

By convention, certain letters are used to specify atomic orbitals. They are *s*, *p*, *d* and *f*. The *s* orbital has a spherical shape, the *p* orbital is like a dumb-bell, while the shapes of *d* and *f* orbitals are much more complicated.

Atoms of different elements are characterized by a definite nuclear charge and by a number of electrons, which is numerically equal to the charge arranged at definite energy levels. The energy levels are, in turn, characterized by *principal quantum number n*. The value of *n* specifies the distance at which an electron shell is from the nucleus, and the energy of electrons in this shell. The higher the value of *n*, the larger is the electron cloud and the higher is the energy of electrons.

The energy levels are made up of a definite number of subshells. The first energy level contains one subshell, the second two, the third three, and so on. A subshell characterizes *azimuthal* (*orbital* or angular momentum) *quantum number* denoted by *l*. This quantum number determines the shape of the electron cloud and specifies the energy of an electron in the subshell. The subshells have the following numerical and alphabetical designations:

s	*p*	*d*	*f*
0	1	2	3

One subshell may contain several electron clouds (orbitals) of the same shape arranged in different directions in space. By convention, the position of an electron cloud is indicated by a square box □. The number of such boxes is determined by *magnetic quantum number m*. Thus, we can have the following picture:

the *s* subshell consists of 1*s* orbital and 2 electrons (s^2)
the *p* subshell consists of 3*p* orbitals and 6 electrons (p^6)
the *d* subshell consists of 5*d* orbitals and 10 electrons (d^{10})
the *f* subshell consists of 7*f* orbitals and 14 electrons (f^{14})

The number of electrons in an orbital is determined by a fourth quantum number called *spin quantum number* and denoted by *s*. It specifies the spinning motion of an electron. An orbital (quantum square box) may contain not more than two electrons.

Electron distribution in various energy levels, subshells and orbitals is depicted in the form of electronic configurations and electron diagrams and obeys three restrictions.

Pauli exclusion principle states that in a given atom no two electrons can have the same set of four quantum numbers.

Principle of lowest energy. According to this principle, electrons should be allotted to various shells and subshells in such a manner that the bonding between an electron and a nucleus be the strongest. In other words, an electron should have the lowest possible energy.

Hund's rules. They are useful to deal with a situation where more than one orbital of equal energy is available to be filled.

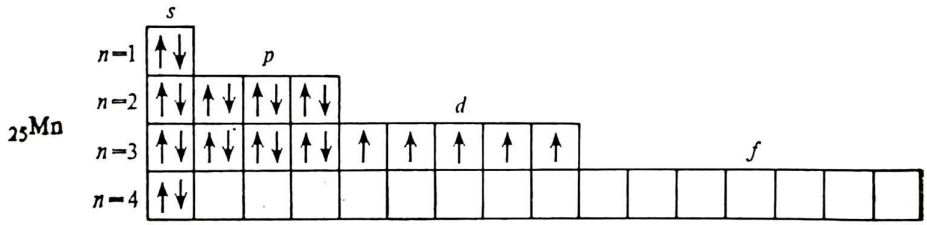
(a) When a group of empty orbitals having equal energies is available, the electrons should first be allotted singly to different orbitals.

(b) When electrons are placed in different equal-energy orbitals, their spins should be parallel.

Thus, for manganese in the ground state, the electronic configuration is

$$_{25}\mathrm{Mn}\quad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$$

and the electron diagram is



In 1932, the English physicist James Chadwick showed that there are rays that consist of electrically neutral particles, which were later termed as neutrons. As a result of a thorough study of nuclear reactions, the Soviet physicists D.D. Ivanenko, E.N. Gapon and the German physicist W. Heisenberg, who worked independently, developed in the year of 1932 a *proton-neutron theory* of the structure of atomic nuclei. This theory states that the atomic nuclei consist of protons and neutrons. Both

types of particles, which are termed as neucleons, have nearly the same mass of 1. Since electrons in an atom have a negligible mass, one can determine the number of neutrons from the difference between the mass of the atom and that of the protons. Mass number is, therefore, equal to the sum of protons and neutrons, while atomic number equals the number of protons in a nucleus or of electrons in an atom. However, in nature atoms of the same element have different atomic masses. For example, hydrogen atoms of three types occur, with masses 1, 2, and 3:

$$^{1}_{1}H \quad ^{2}_{1}H \quad ^{3}_{1}H \text{ or } \underset{\text{protium}}{^{1}_{1}H} \quad \underset{\text{deuterium}}{^{2}_{1}D} \quad \underset{\text{tritium}}{^{3}_{1}T}$$

Nuclei in all the three types contain the same number of protons, but different number of neutrons. In protium, the nucleus contains one proton only, in deuterium one proton and one neutron, while in tritium one proton and two neutrons.

Atoms having the same nuclear charge, but different mass numbers, are called isotopes*.

In Mendeleev's periodic table, the atomic mass of an element is expressed as an average value of the mass numbers of all its isotopes taken in a percent ratio which complies with their abundance in nature. Atoms of different isotopes of the same element have, besides different nuclear properties, the same structure of the electron shell. This is the reason why chemical and physical properties of isotopes are nearly the same. Isotopes occupy the same place in the periodic table.

Isotope transmutation reactions may be represented in the form of nuclear reactions. Equations of such reactions contain symbols for elements with subscripts. The number above such a symbol represents the atomic mass of the respective element, while that below represents the nuclear charge of the atom.

For example, the nuclear reaction that takes place when $^{242}_{94}Pu$ is converted to uranium as a result of an alpha

* Atoms with the same mass numbers, but different nuclear charges are known as *isobars*. The isobar nuclei contain various numbers of protons, hence, carry different charges, and, therefore, occupy different places in Mendeleev's periodic table.

particle emission may be represented by the following equation

$$^{242}_{94}\text{Pu} - ^{4}_{2}\alpha = ^{238}_{92}\text{U}$$

Isotope transmutation reactions occur in accordance with the Group displacement law which states that

the new element formed as a result of emission of an alpha particle from the nucleus of a radioactive element occupies a position two groups to the left of that of the initial element and the new element formed by the emission of a beta particle from the nucleus of a radioactive element occupies a position one group to the right of that of the initial element in the periodic table.

The reason behind such displacements is that in an alpha particle emission the atomic number of the new or daughter element is smaller by 2 units and its mass number is smaller by 4 units than the original or parent element, whereas emission of a beta particle does not cause any change in the mass number of the nucleus, but the atomic number of the new nucleus or of the daughter element corresponding to it will be greater by 1 compared to the parent element. An example of β-emitter is $^{40}_{19}\text{K}$:

$$^{40}_{19}\text{K} - ^{0}_{1} = \beta^{40}_{20}\text{Ca}$$

In nuclear transmutation reactions the mass number and charge are both conserved. For example, when nitrogen atoms are bombarded by alpha particles, protons and the $^{17}_{8}\text{O}$ isotope atoms are produced:

$$^{14}_{7}\text{N} + ^{4}_{2}\text{He} = ^{1}_{1}\text{H} + ^{17}_{8}\text{O}$$

The sum of the upper indices on the left (14 + 4) equals the sum of the upper indices on the right (1 + 17). The same applies to the sum of the lower indices on both sides of the equality sign; i.e. 7 + 2 = 1 + 8.

Example 1. Chlorine has two isotopes with mass numbers 35 and 37. For each isotope, determine the atomic number, the number of protons and neutrons and the nuclear charge. Determine the mass percent of the isotopes in chlorine, taking the atomic mass of chlorine as 35.453.

Solution. Both chlorine isotopes have the atomic number which is 17, hence, the same nuclear charge, i.e. 17 pro-

tons. Now, since the atom, as a whole, is electrically neutral, it must contain 17 electrons as well. According to the proton-neutron theory, the chlorine isotope $^{35}_{17}Cl$ will have $(35 - 17) = 18$ neutrons, while the other isotope with mass number 37 will contain $(37 - 17) = 20$ neutrons. If the mass percent of the isotope $^{35}_{17}Cl$ in naturally occurring chlorine is designated by X and of $^{37}_{17}Cl$ by $(100 - X)$, then we get the following equation

$$\frac{35X + 37(100 - X)}{100} = 35.453, \text{ whence } X = 77.4\%$$

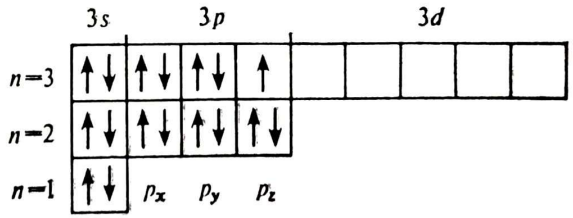
Therefore, chlorine contains 77.4% of $^{35}_{17}Cl$ isotope and 22.6% of $^{37}_{17}Cl$ isotope.

Example 2. Write the electron distribution scheme, the electronic configuration and the electron diagram for a chlorine atom.

Solution. Chlorine lies in the third period, so its atom contains three energy levels. Chlorine belongs to Group VIIA. This means that a chlorine atom has seven electrons in its outermost shell. The number of electrons in the remaining two shells is determined from the formula $N = 2n^2$ and is 2 and 8. Thus, the scheme for the structure of a chlorine atom is

	K	L	M
$_{17}Cl$	2	8	7

its electronic configuration is $_{17}Cl\ 1s^2 2s^2 2p^6 3s^2 3p^5$ and electron diagram is as follows:



Example 3. Characterize chlorine as an element and its compounds with oxygen and hydrogen on the basis of its position in the periodic table.

Solution. Chlorine is arranged in Group VIIA. It is a nonmetal. It has seven electrons in the outermost energy level and exhibits a highest valence of seven in oxygen-containing compounds. Its highest oxide has a formula of

Cl_2O_7 and is acidic in nature. Its hydroxide is an acid, $HClO_4$. With hydrogen, it also forms an acid, HCl. It follows from the electron diagram for chlorine atom that there are several vacant *d* orbitals in the third shell. For this reason, such an atom may exhibit in an excited state the valences of 3, 5 and 7.

Example 4. What are the similarities and what are the differences in the properties of chlorine and manganese compounds?

Solution. Manganese is arranged in the same Group as chlorine and has two electrons in the outermost energy level, which means that it is a metal (all elements arranged in the secondary or B subgroups are metals). It exhibits its lowest valence (two) with oxygen in MnO, a basic oxide, and in $Mn(OH)_2$, a base. Metals do not form compounds with hydrogen (like HCl). Heptavalent manganese, in the same way as chlorine, forms acidic oxide, Mn_2O_7 and acid, $HMnO_4$. Compounds of tetravalent manganese with oxygen possess amphoteric properties.

Example 5. Write the electronic configurations of chromium and copper atoms. Explain why in both cases the fourth shell contains one *s* electron each.

Solution. Chromium (atomic number 24) and copper (atomic number 29) lie in the fourth period and have four electron shells. Starting with Sc, the third subshell of the atoms of these elements is occupied. One, therefore, would expect the following electronic configurations

$$\text{Cr}\ 1s^22s^22p^63s^23p^63d^44s^2 \qquad \text{Cu}\ 1s^22s^22p^63s^23p^63d^94s^2$$

But electrons are actually arranged in the last two subshells of Cr and Cu in the following manner:

$$3d^54s^1 \text{ and } 3d^{10}4s^1$$

This is explained by the comeback of one electron from the 4*s* subshell to the 3*d* one.

PROBLEMS AND EXERCISES

1. By whom and when were electrons, protons and neutrons discovered? What are their masses and charges? What particles does a nucleus of an atom consist o ?

2. What are the main ideas of the nuclear theory of the atomic structure? Mention its shortcomings.

3. What are the main points of the atomic theory of Bohr and Sommerfeld? Mention its drawbacks.

4. What are the main ideas behind the quantum-mechanical theory of the structure of atoms?

5. An element X has a higher oxide, X_2O_5. Its outermost quantum shell contains one electron. State whether such an element can form a gaseous compound by reacting with hydrogen.

6. How many subshells are there in the second, third and fourth quantum shells?

7. What is the maximum number of electrons that the *s*, *p*, *d* and *f* subshells can accommodate?

8. In which Groups and in which subgroups of the periodic table are the *s* and *p* elements arranged?

9. What is the energy capacity of (a) the energy shells *K* and *N*, (b) energy subshells *s* and *d*?

10. Which state of an atom is termed as the ground state and which as excited one?

11. State the modern formulation of the Mendeleev periodic law.

12. How would you account for periodicity in the properties of elements?

13. How does the theory of atomic structure explain the rise in nonmetallic properties of elements within a period with increasing atomic number?

14. In terms of the theory of the structure of atoms, how would you account for the rise in metallic properties of elements with increasing atomic mass down a Group?

15. Why most of the elements of the periodic table have fractional values for their atomic masses?

16. In which particles do the nuclei of isotope atoms of an element differ from one another?

17. What is common to the isotopes of one and the same element?

18. What do you understand by nuclear transmutation reactions?

19. What changes take place in atomic mass as a result of radioactive decay?

20. It is known that radium is a radioactive element. Then how would you explain that it is still found in nature?

21. State: (a) the total number of nucleons, (b) the num-

ber of protons and neutrons in the nucleus, and (c) the total number of electrons in the atom of $^{45}_{21}Sc$, $^{79}_{34}Se$, and $^{131}_{54}Xe$.

22. The atomic nucleus of an element contains 45 neutrons and the electron shell of its atom 34 electrons. What element is it and what is the nuclear charge of the atom?

23. The mass of an atom of certain isotope equals 127 amu. There are 53 electrons in the electron shell of the atom. What element is it and how many protons and how many neutrons are there in the atomic nucleus?

24. Carbon has two isotopes with mass numbers 12 and 13. Indicate for each of them the atomic number, the number of protons and of neutrons and the nuclear charge.

25. The atomic mass for boron is 10.81. Boron has two isotopes, $^{10}_{5}B$ and $^{11}_{5}B$. Determine the mass percent of $^{11}_{5}B$ in it.

26. How many neutrons do the nuclei of the following isotopes contain: $^{16}_{8}O$, $^{17}_{8}O$, $^{18}_{8}O$, $^{35}_{17}Cl$, $^{37}_{17}Cl$, $^{68}_{30}Zn$, $^{64}_{30}Zn$, $^{32}_{16}S$, $^{33}_{16}S$, $^{34}_{16}S$, $^{36}_{16}S$?

27. Naturally occurring chlorine contains nearly three atoms of the isotope $^{35}_{17}Cl$ per each atom of the isotope $^{37}_{17}Cl$. What is the average atomic mass of natural chlorine?

28. Determine the relative atomic mass of magnesium, if the mass percent of its isotopes $^{24}_{12}Mg$, $^{25}_{12}Mg$ and $^{26}_{12}Mg$ in earth's crust is 78.60, 10.11 and 11.29%, respectively.

29. Copper has two isotopes with mass numbers 65 and 63. Mention for each isotope the atomic number, the number of protons and neutrons and the nuclear charge. Taking the relative atomic mass of copper as 63.54, determine the mass percent of the isotope with mass number 65. What is the mass percent of the isotope Cu-65 in cupric hydroxide?

30. The mass percents of silver isotopes are: 44% $^{109}_{47}Ag$ and 56% $^{107}_{47}Ag$. Determine the relative atomic mass for silver.

31. Unstable isotope, $^{25}_{11}Na$, emits a beta particle. The nucleus of which element is it converted to?

32. Isotope $^{11}_{5}B$ emits an alpha particle. The nucleus of which element is it converted to?

33. Under the action of neutrons and by capturing two beta particles, thorium-232 is converted into an excellent

nuclear fuel. What fuel is it? Write down the equations to represent these nuclear transmutation reactions.

34. How many alpha and beta particles should the lead isotope, $^{208}_{82}Pb$, lose to be converted to a mercury atom, $^{200}_{80}Hg$?

35. What element will be formed on natural decay of a radium nucleus: $^{226}_{88}Ra = ? + {}^{4}_{2}\alpha$?

36. On successive disintegration of polonium, three alpha and two beta particles are emitted. What element is formed in this case? State its oxygen valence and hydrogen valence, atomic mass and nuclear charge.

37. State whether the rule of equality for the sum of subscripts has been observed in each of the following nuclear reactions: (a) $^{222}_{86}Rn + {}^{4}_{2}He \rightarrow {}^{226}_{88}Ra$; (b) $^{19}_{9}F + {}^{4}_{2}He \rightarrow {}^{22}_{10}Ne + {}^{1}_{1}H$; (c) $^{25}_{11}Na + \beta \rightarrow {}^{25}_{12}Mg$.

38. On successive disintegration, $^{247}_{96}Cm$ emits three alpha particles, three beta particles and two neutrons, $^{1}_{0}n$, and forms an element. Which Group of the periodic table does the element belong to? What are the nuclear charge and atomic mass of the element thus formed?

39. On the basis of the structure of atoms prove which of the two Group II elements, magnesium or strontium, exhibits stronger metallic properties.

40. What is common in the atomic structures of lithium, sodium and potassium?

41. Which atoms in Group I contain in their penultimate shells 8 and 18 electrons, respectively.

42. Write the electronic configurations for the following ions: Fe^{2+}, Fe^{3+}, Cl^{-}, S^{2-}, Cu^{2+}, and Cr^{3+}.

43. Is it possible for a bivalent metal ion to exhibit an electronic configuration of the type $1s^22s^22p^63s^1$ or $1s^22s^22p^63s^23p^6$?

44. On the basis of electronic configurations, determine the chemical properties of elements with atomic numbers 7, 17, 20 and 26.

45. How many electron shells are there in atoms having, respectively 4, 9, 17 and 19 protons in their nuclei? Explain your answer.

46. Is it true for all elements that the Group number corresponds to the number of electrons in the outermost shell of the atom? Explain your answer.

47. How many unpaired electrons does the electron

shell of chlorine, sulphur, and carbon atoms contain in their ground states?

48. An element X has the highest oxide of the formula X_2O_7 and contains $4p^5$ electrons in the outermost quantum shell. Does the element react with hydrogen to form a gaseous compound? Write down the electronic configuration of the element.

49. Indicate which of the following configurations are real and which are not: (a) $1p^2$, (b) $4s^2$, (c) $5f^4$, (d) $3d^3$, (e) $4p^5$, (f) $2p^4$, and (g) $3d^8$.

50. For the following configurations, indicate which subshells are completely filled and which ones are not filled with electrons up to their full capacity: (a) $3s^2$, (b) $5d^8$, (c) $4f^{14}$, (d) $6s^1$, (e) $2p^6$ and (*f*) $3d^{10}$.

51. Write down the electronic configuration for the atom of each element arranged in (a) Group VI and third period, (b) Group IV, fifth row and fourth period, (c) Group VII, seventh row and fifth period.

52. Name the elements belonging to fourth, fifth and sixth periods, whose *d* orbitals have just been filled ($3d^{10}$, $4d^{10}$, $5d^{10}$).

53. Write down the electronic configurations for atoms belonging to the fourth period and Group VII.

54. Name the elements with the following electronic configurations:

(a) $1s^22s^22p^63s^23p^5$, (b) $1s^22s^22p^63s^23p^64s^1$,

(c) $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^55s^1$

55. Write down the electronic configuration of an iron atom. How are electrons distributed in the *d* subshell and what is the highest valence of iron?

56. Name the elements which have one electron in $3d$ and $4d$ subshells, respectively. Write down the electronic configurations of the atoms of these elements and indicate their positions in the periodic table.

57. On the basis of the electron distribution in orbitals for a silicon atom in an excited state, how would you account for the valence of four exhibited by this element?

58. Illustrate the applicability of Hund's rules using manganese and arsenic as examples.

59. The main subgroup of Group VIII (i.e. Group VIIIA) consists of the so-called noble gases. Three of

these, helium, neon and argon are inert gases, while the rest form chemical compounds. On the basis of the electron diagrams, explain why one of the three elements, i.e. helium, neon and argon can form compounds, whereas the remaining two cannot.

60. Name the elements which have one electron in $3p$ and $4p$ subshells, respectively. Write down the electronic configurations for the atoms of these elements and indicate their positions in the periodic table.

61. How many vacant d orbitals are there in a vanadium atom? Write down the electronic configuration and electron diagram for it.

62. Using Hund's rules, show the electron distribution in quantum square boxes (orbitals) for chromium, cobalt and nitrogen atoms.

63. Write the electron diagram for a chlorine atom. How many electron pairs are there and which orbitals do they occupy? How many unpaired electrons are there in the atom?

64. State whether a given shell may have d electrons, if it ends with any one of the following configurations: $3s^1$, $4p^1$ or $5f^{11}$.

65. Build up the electronic configurations for the atoms of cesium, lanthanum, tantalum and lead. Which elements (s, p, d or f) do they belong to?

1.5 TYPES OF CHEMICAL BOND. OXIDATION NUMBER. OXIDATION-REDUCTION (REDOX) REACTIONS

From the atomic structure viewpoint all elements may be divided into two groups: elements having completely filled outermost quantum shells (the inert gases) and elements with unfilled outermost shells, that is, the remaining elements.

Elements with completely filled shells are chemically inert under ordinary conditions, while the rest are active. Each atom tends to be like the inert gases, that is, to have outermost shells completely filled (to have octets, in other words). To achieve such a state, atoms either lose or gain electrons (theory of W. Kossel, 1916).

The behaviour of atoms in chemical reactions depend

upon how tightly their electrons are held in orbitals. The energy required to move an electron from an atom in the ground state is termed as *ionization potential.* It is measured in electron volts (eV). One eV is equivalent to 96.6 kJ/mole.

Multielectron atoms have several ionization potentials corresponding to the removal of first, second, and so on electrons. For example, the removal of second electron from a lithium atom requires a huge energy of 6960 kJ/mole. This is the reason why in its compounds lithium is monovalent.

Atoms which contain 1, 2 or 3 electrons in the outermost orbits give off their electrons most readily, so that after such a removal, the atoms are left with an octaelectronic shell (an octet).

While going from left to right across a period, one can observe an increase in the ionization potential. This is because the nuclear charge increases within a period, whereas the atomic radius changes very little.

Negatively charged particles are formed when an electron is added to a neutral atom. The energy required for adding an electron to an atom is called *electron affinity.* Halogen atoms have the highest electron affinity: Cl (3.81), Br (3.56), I (3.29), and S (2.33). Electron affinity increases from left to right across a row and, as a rule, decreases down a subgroup.

Those atoms add electrons most readily which require only a few electrons (one to four) to make an octaelectronic outermost shell, that is, elements which contain 7, 6, 5, 4 electrons in the outermost shell.

Addition of an electron to oxygen, sulphur, nitrogen, etc. atoms results in an energy release. When other electrons are added, energy is to be supplied, because the negative ion already formed repels the in-coming electrons.

The sum of ionization potential and electron affinity is called *electronegativity.* This concept may be used for determining the type of chemical bond and oxidation number of atoms in a compound. The electronegativity table (Table 1.1) proposed by L. Pauling is widely used nowadays.

Using the table of relative electronegativity, one can judge not only of electron displacement towards a more

Table 1.1 Relative Electronegativity of Elements

H 2.1							
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	In 1.5	Sn 1.8	Sb 1.9	Tl 2.1	I 2.15

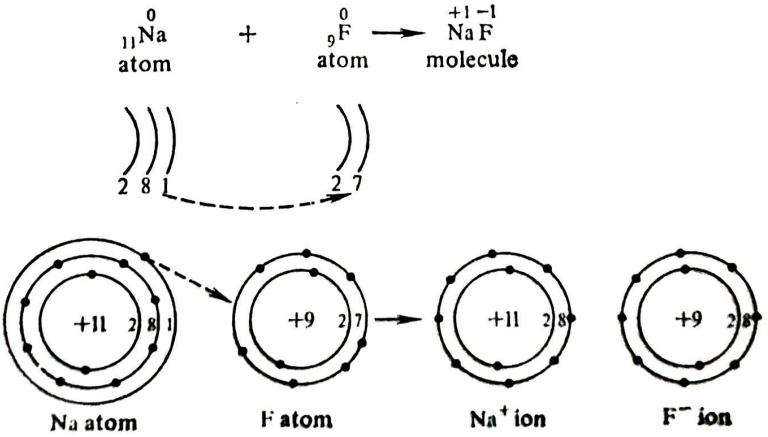
electronegative atom during the interaction of atoms, but also draw a conclusion about the type of a chemical bond (covalent or ionic) and its polarity. When the electronegativity difference (ΔEN) between two atoms forming a chemical bond is greater than 1.9 the bond is ionic, if the difference is less than 1.9, it is covalent. For example, for

K—Cl, $\Delta EN = 3.0 - 0.9 = 2.1 > 1.9$, so the bond is ionic

Be—Cl, $\Delta EN = 3.0 - 1.5 = 1.5 < 1.9$, so the bond is polar covalent

Cl—Cl, $\Delta EN = 3.0 - 3.0 = 0$, so the bond is nonpolar covalent

Ionic bond. Let us now consider the formation of a sodium fluoride molecule on the basis of the above considerations:



The last electron in a sodium atom (in the *M* shell) is bound to the nucleus not very tightly. On the other hand, a fluorine atom has seven electrons in the *L* shell. An additional electron may be added to it to complete its outermost shell. Indeed, when a sodium atom and a fluorine atom approach each other, the last electron of sodium may pass over to the fluorine atom forming thereby a molecule of sodium fluoride, which consists of a sodium cation and a fluoride anion. These two ions are held together by attraction forces between the oppositely charged ions.

When an atom is converted into a positively charged ion (cation) its size decreases, whereas negatively charged ions (anions) have a larger size than the corresponding atom, since the bonds between the electrons and the nucleus weaken due to repulsion of the excess negative charge by the nucleus. The chemical bond formed between two oppositely charged ions is called *ionic bond*. Such a bonding is brought about via coulombic forces of attraction.

Ions are charged particles formed from atoms by giving away or taking up electrons.

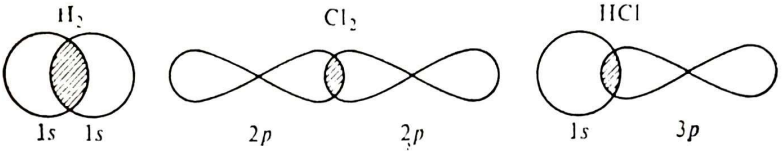
An ionic bond is formed between atoms of metals and nonmetals. Electrons are shifted from the outermost shells of metals to those of nonmetals. There are comparatively few ionic compounds. Most organic compounds and many inorganic compounds do not have ions in their molecules.

Covalent bond. In the year of 1916, the American scientist G.N. Lewis devised the theory of covalent bond. Like W. Kossel, he also believed that atoms tend to acquire an octaelectronic outermost shell, that is, an electronic octet (an electronic doublet in the case of hydrogen atom).

Formation of a chemical bond between atoms is possible when their valence electrons form pairs (doublets) that are shared between both atoms. Electrons of such pairs revolve in the field of nuclei of both atoms in the so-called *molecular orbits*.

Electrons form such pairs only when their spins are opposite. Pairing of electrons with opposite spins is accounted for by the fact that the "cloud" of one electron penetrates into the space occupied by the "cloud" of an-

other electron. As a result of such an overlap, a region of increased electron density is formed between nuclei of the bonding atoms. This brings the nuclei nearer, and a bond arises between the atoms as shown below:



So during the formation of a molecule, the electrons belonging to two different nuclei become common to both of them to form a single electron cloud. Such a bielectronic bond belonging simultaneously to two nuclei is called *covalent bond* and is conventionally designated by dashes: F—F, O=O, and so on.

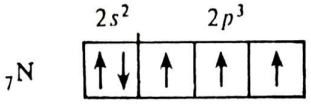
When a molecule is produced from similar atoms, the density of the electron cloud is found to be symmetrical relative to the nuclei of both atoms. Such a covalent bond is termed as *nonpolar* or *homopolar bond.* If, on the other hand, two different atoms form the molecule, then the molecular cloud is shifted towards the more electronegative atom. Such a covalent bond is known as *polar* or *heteropolar bond.* For example, in a hydrogen chloride molecule the common electron pair is shifted towards the chlorine atom:

As a result, the chlorine atom acquires an extra negative charge called effective charge, while the hydrogen atom acquires effective positive charge, equal in magnitude, but opposite in sign.

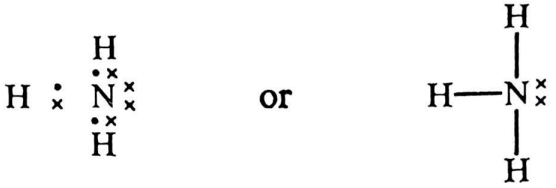
Coordinate or donor-acceptor bond. Formation of simple compounds is explained by the formation of ionic and atomic bonds. But there are cases when two compounds react with each other to yield a molecular complex. An example is the formation of ammonium chloride from ammonia and hydrogen chloride:

$$NH_3 + HCl \rightarrow NH_4Cl$$

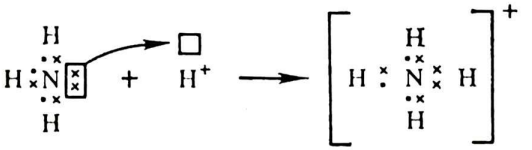
Let us consider the electronic structure of an ammonia molecule. The nitrogen atom in such a molecule has five electrons in the outermost energy shell, that is $2s^2\,2p^3$:



Three unpaired electrons are shared by three hydrogen atoms to form three covalent bonds:



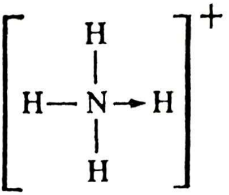
From the electronic structure of ammonia molecule it follows that the nitrogen atom has one electron pair ($2s^2$), which has not taken part in any chemical bond formation. This is the so-called *unshared electron pair.* This electron pair permits to form a new chemical bond between the nitrogen atom of ammonia molecule and, say, a hydrogen ion:



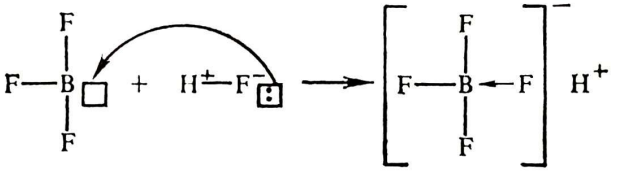
This new bond arises when the vacant quantum box of the hydrogen ion is filled by the unshared electron pair, which belonged earlier to the nitrogen atom.

The covalent bond formed between two atoms at the expense of an unshared electron pair of one atom (donor) and a vacant orbital of another atom (acceptor) is called *donor-acceptor* or *coordinate bond.* It should be pointed out here that a donor-acceptor bond differs from an ordinary covalent bond only in the source of the common electron pair, but not in properties.

In schemes (structural formulas) the donor-acceptor bond is designated by an arrow:



When a BF_3 molecule reacts with an HF molecule, the fluoride ion of the HF molecule donates an unshared electron pair to a boron having a vacant *p* orbital. As a result, a molecule is formed which contains a donor-acceptor bond, B being the acceptor and F^- (from the HF molecule) the donor:



Oxidation number. To characterize the state of an atom in a molecule, the concept of *oxidation number* is introduced instead of the concepts of positive and negative valences and covalence.

Oxidation number is the formal charge on an atom in a molecule, calculated assuming the molecule to consist of ions only.

Oxidation number is represented by Arabic numbers with a plus or minus sign in front of them. The algebraic sum of the oxidation numbers of all the atoms in a molecule always equals zero. Thus, in an Na_2CO_3 molecule, Na has an oxidation number +1, C +4, and O −2:

$+1$	$+4$	-2
Na_2	C	O_3
$+1\times2$	$+4$	-2×3

To determine the oxidation numbers of elements in compounds, one should not forget that electrons are shifted to the atom of more electronegative element. For example, in PCl_3, the phosphorus atom has an oxidation

number of +3, while chlorine —1, since the electronegativity of the former is 2.1, whereas that of the latter is 3.0. In Cl_2O, the chlorine atom has a lower electronegativity than the oxygen atom (3.5). This is why the chlorine atom in this compound will have an oxidation number of +1, while the oxygen atom —2.

In many cases the oxidation number is not equal to the valence of the given element. For example, in the following compounds

$$\overset{-2}{H_2O} \quad \overset{-1}{H_2O_2} \quad \overset{0}{O_2} \quad \overset{+2}{OF_2}$$

oxygen has different oxidation numbers. To determine the valence and oxidation number, it is necessary in such cases to draw graphic formulas. For instance, in FeS_2, whose graphic formula is , sulphur and iron both have the same valence of two, while the oxidation numbers of sulphur and iron are, respectively, —1 and +2. In CaC_2 or , carbon has a valence of 4, and an oxidation number —1.

Oxidation-reduction (redox) reactions. All chemical reactions are divided into two types: reactions taking place with a change, and without a change in the oxidation number.

Reactions resulting in a change in the oxidation numbers of elements are termed as oxidation-reduction or redox reactions.

Redox equations may be designed in several ways. Here, let us discuss the *ion-electron method* for balancing a redox equation. It is based on determining the total number of migrating electrons. The following example will illustrate the use of this method

$$\overset{-2}{Mn}\overset{+5}{S} + HNO_3 \rightarrow \overset{+6}{Mn}\overset{+4}{S}O_4 + NO_2 + H_2O$$

First, we determine the atoms that have changed their oxidation numbers: $S^{-2} \rightarrow S^{+6}$ and $N^{+5} \rightarrow N^{+4}$. Next, we

determine the number of lost and gained electrons:

$$\overset{-2}{S}\ (\text{lost}) - 8e^- \rightarrow \overset{+6}{S}; \quad \overset{+5}{N}\ (\text{gained}) + e^- \rightarrow \overset{+4}{N}$$

Now, the number of lost and gained electrons should be the same. So we can write the two half-reactions as follows:

Reducing agent	$\overset{-2}{S} - 8e^- \rightarrow \overset{+6}{S}$	$\times 1 =$	$\overset{-2}{S} - 8e^- \rightarrow \overset{+6}{S}$; oxidation
Oxidizing agent	$\overset{+5}{N} + e^- \rightarrow \overset{+4}{N}$	$\times 8 =$	$8\overset{+5}{N} + 8e^- \rightarrow 8\overset{+4}{N}$; reduction

The least common multiple in this example is 8. Then we put the final coefficients at the oxidizing and reducing agents into the redox equation and thus get

$$\overset{-2}{MnS} + 8\overset{+5}{HNO_3} = \overset{+6}{MnSO_4} + 8\overset{+4}{NO_2} + 4H_2O$$

The process of conversion of sulphur with an oxidation number of -2 in MnS into that with $+6$ in $MnSO_4$ is an electron donating process, i.e. oxidation. On the other hand, the process of conversion of nitrogen with an oxidation number of $+5$ in HNO_3 into that with $+4$ in NO_2 is called reduction. The substance, MnS, in this case is a reducing agent or reductant, while HNO_3 an oxidizing agent or oxidant.

Let us now consider another more complex example, namely, the reaction of arsenic sulphide with nitric acid:

$$As_2S_3 + HNO_3 \rightarrow H_3AsO_4 + H_2SO_4 + NO$$

Again, we determine the oxidizing and reducing agents of the given reaction. While writing the half-reaction equations, the subscripts present in the molecular formula of the reducing agent (As_2O_3) should be included into the equations. Thus we get

Red. agent	$\overset{+3}{2As} - 4e^- \rightarrow \overset{+5}{2As}$	$\times 3 =$	$6\overset{+3}{As} - 12e^- \rightarrow 6\overset{+5}{As}$; oxidation
Red. agent	$3\overset{-2}{S} - 24e^- \rightarrow 3\overset{+6}{S}$	$\times 3 =$	$9\overset{-2}{S} - 72e^- \rightarrow 9\overset{+6}{S}$; oxidation
Ox. agent	$\overset{+5}{N} + 3e^- \rightarrow \overset{+2}{N}$	$\times 28 =$	$28\overset{+5}{N} + 84e^- \rightarrow 28\overset{+2}{N}$; reduction

Here the least common multiple is 84 (28×3). Now we put the final coefficients 3 and 28 into the redox equation and then balance all the elements with the exception of

H and O:

$$3As_2S_3 + 28HNO_3 \rightarrow 6H_3AsO_4 + 9H_2SO_4 + 28NO$$

Hydrogen and oxygen atoms should be balanced at the last moment by adding H_2O to that part of the equation which lacks these atoms. Thus we get the final equation

$$3As_2S_3 + 28HNO_3 + 4H_2O = 6H_3AsO_4 + 9H_2SO_4 + 28NO$$

Here As_2S_3 is the reducing agent and HNO_3 the oxidizing agent.

Oxidizing and reducing agents. *Oxidizing agents.* The electron affinity of an atom or ion, i.e. their ability to accept electrons is a measure of their oxidizing power. Oxidizing agents may be classified as below:

1. All nonmetal atoms are oxidizing agents. Halogen atoms are the strongest of them, because they are capable of accepting only one electron. As the Group number decreases, the oxidizing power of nonmetal atoms arranged in it decreases as well. The nonmetal atoms of Group IV are, therefore, the weakest oxidizing agents. While going down a Group, the oxidizing properties of the nonmetal atoms decrease due to an increase in the atomic radii.

2. The oxidizing properties of compounds depend on the oxidation numbers of atoms involved in them. Atoms in their highest oxidation states may function as oxidizing agents only. A few examples of them are $K\overset{+7}{Mn}O_4$, $K_2\overset{+6}{Cr}_2O_7$, $K_2\overset{+6}{Cr}O_4$, $\overset{+4}{Pb}O_2$ and so on.

Metal ions with highest oxidation numbers, such as Hg^{2+}, Fe^{3+}, Cu^{2+} and others also act as oxidizing agents.

3. Nitric (HNO_3) and conc. sulphuric (H_2SO_4) acids are oxidizing agents.

Reducing agents. The ionization potential of atoms or ions, that is, their ability to give up electrons is a measure of their reducing power. Reducing agents are classified as follows.

1. Atoms of all elements with the exception of He, Ne and Ar may function as reducing agents. Those elements lose electrons more readily, which have 1, 2 or 3 electrons in their outermost shells.

2. Positively charged metal ions with lowest oxidation numbers such as Fe^{2+}, Cr^{3+}, Mn^{2+}, Sn^{2+}, Cu^{+} also act as reducing agents.

3. Finally, negatively charged ions like Cl^{-}, Br^{-}, I^{-}, S^{2-} are also reducing agents.

Classification of oxidation-reduction (redox) reactions. Depending upon whether an electron migration takes place between the atoms of the same or different compounds, all redox reactions are divided into three types: intermolecular, intramolecular, and disproportionation redox reactions.

Those reactions are called *intermolecular redox reactions* in which the oxidants and the reductants belong to different substances. This may be illustrated by the following redox reaction:

$$\overset{+6}{2H_2SO_4}\,(\text{conc.}) + \overset{0}{Cu} = \overset{+2}{CuSO_4} + \overset{+4}{SO_2} + 2H_2O$$

$$\begin{array}{lll} \text{Reducing agent} & \overset{0}{Cu} - 2e^- = \overset{+2}{Cu} & \times 1 \\ \text{Oxidizing agent} & \overset{+6}{S} + 2e^- = \overset{+4}{S} & \times 1 \end{array}$$

In *intramolecular redox reactions* both oxidizing and reducing agents are different atoms of one and the same molecule:

$$\overset{+5\,-2}{2KClO_3} = \overset{-1}{2KCl} + \overset{0}{3O_2}$$

$$\begin{array}{lll} \text{Oxidizing agent} & \overset{+5}{Cl} + 6e^- = \overset{-1}{Cl} & \times 2 \\ \text{Reducing agent} & \overset{-2}{3O} - 4e^- = \overset{0}{O_2} & \times 3 \end{array}$$

In *disproportionation reactions* atoms of one and the same element function as both oxidizing and reducing agents:

$$\overset{0}{Cl_2} + H_2O = \overset{+1}{HClO} + \overset{-1}{HCl}$$

$$\begin{array}{lll} \text{Oxidizing agent} & \overset{0}{Cl} + 1e^- = \overset{-1}{Cl} & \times 1 \\ \text{Reducing agent} & \overset{0}{Cl} - 1e^- = \overset{+1}{Cl} & \times 1 \end{array}$$

PROBLEMS AND EXERCISES

1. What is an ion? Which chemical bond is termed as ionic or electrovalent?
2. Between atoms of which elements is an ionic bond formed?
3. What is a covalent bond? Which types of a covalent bond are distinguished?
4. Between atoms of which elements is a covalent bond formed?
5. Which molecules are called (a) polar, (b) nonpolar and (c) ionic?
6. Give a short definition of a donor-acceptor chemical bond.
7. Which of the following compounds displays the highest bond polarity: CH_4, NH_3, H_2O or HF?
8. Which of the following elements is the most electronegative: chlorine, bromine, sulphur, nitrogen or phosphorus?
9. What are the similarities and what are the differences between covalent and coordinate bonds?
10. Towards which elements are the electron pairs shifted in the molecules of the following substances: PCl_3, BF_3, CS_2, CCl_4 and Cl_2O?
11. In which direction is the electron density shifted during the formation of the following bonds: (a) P—H, (b) Br—C, (c) S=O, (d) N—Cl and (e) Si—S?
12. What are the features of a coordinate bond? In which compounds does it exist?
13. Define oxidation number.
14. Which reactions are termed as oxidation-reduction (redox) reactions?
15. Which substances are called oxidizing and reducing agents?
16. How do oxidation numbers change for oxidizing and reducing agents in the course of a redox reaction?
17. Which of the following substances exhibit (a) predominantly oxidizing properties, (b) predominantly reducing properties: chlorine, ferrous sulphate, potassium permanganate, sodium sulphide, nitric acid, sulphur trioxide, carbon and water?

18. How is it possible to judge of the nature of a bond between atoms in a molecule on the basis of relative electronegativity?

19. Determine the number of electrons donated in the following conversions:

$$Cu \rightarrow \overset{+2}{Cu},\ Cr \rightarrow \overset{+6}{Cr},\ Fe \rightarrow \overset{+3}{Fe} \text{ and } Sn \rightarrow \overset{+4}{Sn}$$

20. Determine the number of electrons accepted in the following conversions:

$$P \rightarrow \overset{-3}{P},\ I \rightarrow \overset{-1}{I},\ S \rightarrow \overset{-2}{S} \text{ and } C \rightarrow \overset{-4}{C}$$

21. Determine the oxidation numbers for the following formal ions after 2 electrons have been added to each of them:

$$\overset{+5}{N},\ \overset{+4}{Pb},\ \overset{+7}{Cl},\ \overset{+6}{Se},\ \overset{+3}{Tc} \text{ and } \overset{+2}{Cu}$$

22. Determine the number of lost or acquired electrons in the following conversions:

$$\overset{0}{X} \rightarrow \overset{-2}{X},\ \overset{+5}{X} \rightarrow \overset{+2}{X},\ \overset{-2}{X} \rightarrow \overset{+6}{X},\ \overset{+5}{X} \rightarrow \overset{-3}{X},$$

$$\overset{-2}{X} \rightarrow \overset{0}{X},\ \overset{+7}{X} \rightarrow \overset{+4}{X},\ \overset{0}{X} \rightarrow \overset{+2}{X},\ \overset{+5}{X} \rightarrow \overset{0}{X}$$

23. Illustrate with the help of half-reaction equations the processes of formation from atoms of the following compounds containing ionic bonds: ZnS, MgI_2, PbO_2 and $AlCl_3$.

24. Express the chemical bond formation in the molecules of the following compounds: SiF_4, F_2O, NCl_3, C_2H_2 and C_2H_4.

25. Draw the structural formulas and show the octet formation in NH_3, N_2, $CHCl_3$, HCl, H_2CO_3.

26. Cite three examples when one and the same element forms ionic, polar covalent and nonpolar covalent bonds.

27. Give examples of molecules (two in each case) in which the bonds between atoms are formed by one, two and three electron pairs, respectively.

28. Draw structural and electronic formulas for compounds of phosphorus with (a) hydrogen, (b) chlorine and (c) boron.

29. Draw structural and electronic formulas for hydrides of (a) selenium, (b) iodine and (c) nitrogen.

30. Electrons of which shell take part in the bond formation in the covalent compounds, H_2, Cl_2, O_2 and N_2?

31. By consulting a table of relative electronegativities calculate the electronegativity differences for bonds, K—Cl, H—O, Cl—O, Fe—Cl, Na—F, Cl—Cl, C—Br, H—P and C—F and characterize these bonds.

32. Which of the following bonds is the most ionic: K—Cl, Ca—Cl, Fe—Cl or Ge—Cl?

33. Which of the following bonds is the most covalent: Li—F, Be—F, B—F or C—F?

34. Which of the ions, Mg^{2+}, Fe^{2+}, S^{2-}, Cl^-, Cu^+ and Cr^{3+} have noble gas configurations and may function as reducing agents in oxidation-reduction (redox) reactions?

35. In compounds, KCl, CO_2, OF_2, H_2O and BF_3 the common electron pairs are shifted towards which atoms?

36. Which ions constitute the following substances: CaS, $ZnCl_2$, KBr and Na_2S? Draw the electronic formulas of these molecules.

37. What types of chemical bonds have the molecules of NaCl, N_2 and H_3P? Determine the oxidation numbers of elements in these compounds.

38. Which atom or ion serves as the donor of an electron pair during the formation of the $[BF_4]^-$ ion?

39. Determine the covalences and oxidation numbers for nitrogen in its compounds: KNO_3, $NaNO_2$, N_2 and H_3N.

40. Determine the covalences and oxidation numbers for elements (carbon, chlorine, and hydrogen) in the following pairs of compounds: (a) CH_4 and CO_2, (b) HCl and HClO, (c) H_2O and CaH_2.

41. Cite examples of reactions in which the oxidation number of sulphur does not change.

42. Calculate the oxidation numbers of manganese in the following compounds: $MnSO_4$, Na_2MnO_4, MnO_3, Mn_2O_7, $KMnO_4$ and H_2MnO_3.

43. Give the half-reaction equations for the reactions of arsenic with (a) potassium, (b) strontium and (c) aluminium.

44. Determine the nature of bonds in the molecules of $SiBr_4$, PBr_3 and Br_2O, and indicate for each of them the

oxidation number and the direction in which the electron density shifts.

45. Determine the oxidation numbers of (a) phosphorus in H_3PO_4, $Ca(H_2PO_4)_2$, P_2O_5 and Mg_3P_2, (b) copper in Cu_2O, $Cu(NO_3)_2$, $(CuOH)_2CO_3$ and $CuCl$, (c) sulphur in K_2SO_3, $Mg(HS)_2$, $KAl(SO_4)_2$ and FeS_2, (d) nitrogen in $NaNO_2$, NH_4NO_3, Ca_3N_2 and N_2O, (e) mercury in HgO, Hg_2O, $HgCl_2$ and $Hg_2(NO_3)_2$.

46. Write the oxidation numbers over the atoms of elements in $K_2B_4O_7$, $CaMnO_4$, $NaClO_4$, $Sn(SO_4)_2$, and $Na_2Cr_2O_7$.

47. Indicate in which of the following cases there takes place:

(a) an oxidation: $HNO_2 \rightarrow HNO_3$, $PbO_2 \rightarrow PbSO_4$, $HClO_4 \rightarrow ClO_2$,

(b) a reduction: $KMnO_4 \rightarrow MnO_2$, $SO_2 \rightarrow K_2SO_4$, $NaBrO_3 \rightarrow Br_2$.

48. For the following redox reactions indicate the oxidizing and reducing agents and write the equations to represent half-reactions:

$$H_2 + Cl_2 = 2HCl \qquad H_2 + 2Na = 2NaH$$
$$O_2 + 2Na = Na_2O_2 \qquad Cl_2 + 2Na = 2NaCl$$

49. Taking into account that chromium (VI) is reduced to chromium (III) sulphate, complete the following redox equations:

$$Al + K_2Cr_2O_7 + H_2SO_4 \rightarrow Al_2(SO_4)_3 + \ldots$$
$$NaNO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow NaNO_3 + \ldots$$
$$H_2S + K_2Cr_2O_7 + H_2SO_4 \rightarrow S + \ldots$$

50. Taking account of the fact that concentrated sulphuric acid is reduced to SO_2 by less active (heavy) metals and to H_2S by active (light) metals, complete the following equations:

$$Zn(act.) + H_2SO_4(conc.) \rightarrow \ldots$$
$$Ag(inact.) + H_2SO_4(conc.) \rightarrow \ldots$$
$$Hg(inact.) + H_2SO_4(conc.) \rightarrow \ldots$$
$$Ca(act.) + H_2SO_4(conc.) \rightarrow \ldots$$

51. Taking into account that while reacting with nonmetals, nitric acid is reduced to NO, complete the follow-

ing redox equations:

$$P + HNO_3 + H_2O \rightarrow H_3PO_4 + \ldots$$
$$C + HNO_3 \rightarrow CO_2 + \ldots$$
$$S + HNO_3 \rightarrow SO_2 + \ldots$$

52. Taking account of the fact that concentrated nitric acid is reduced to NO_2 and diluted HNO_3 to NO, complete the following redox equations:

$$Ni + HNO_3(dil.) \longrightarrow Ni(NO_3)_2 + \ldots$$
$$B + HNO_3(conc.) \longrightarrow H_3BO_3 + \ldots$$
$$Na_2S + HNO_3(dil.) \longrightarrow S + \ldots$$
$$Mn + HNO_3(conc.) \longrightarrow Mn(NO_3)_2 + \ldots$$
$$As + HNO_3(dil.) \xrightarrow{+H_2O} H_3AsO_4 + \ldots$$

53. Adding water to that part of the equation where it is insufficient, complete the following redox equations:

$$Al + NaOH \rightarrow NaAlO_2 + H_2$$
$$Si + KOH \rightarrow K_2SiO_3 + H_2$$
$$H_3AsO_3 + HNO_3 \rightarrow H_3AsO_4 + NO$$

54. Determine the oxidizing and reducing agents, their oxidation numbers and put the required coefficients in the following redox equations:

$$MnO_2 + KClO_3 + KOH \rightarrow K_2MnO_4 + KCl + H_2O$$
$$CuCl_2 + SO_2 + H_2O \rightarrow CuCl + HCl + H_2SO_4$$
$$HgS + HNO_3 + HCl \rightarrow HgCl_2 + S + NO + H_2O$$
$$SnCl_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow Sn(SO_4)_2 + SnCl_4 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$
$$AsH_3 + AgNO_3 + H_2O \rightarrow H_3AsO_4 + Ag + HNO_3$$
$$Zn + KNO_3 + KOH \rightarrow K_2ZnO_2 + NH_3 + H_2O$$

55. Balance the following redox reactions in which both oxidizing and reducing agents are present in one and the same compound (intramolecular redox reactions):

$$Hg(NO_3)_2 \rightarrow Hg + NO_2 + O_2; \quad NH_4NO_3 \rightarrow N_2O + H_2O$$
$$KClO_3 \rightarrow KCl + O_2; \quad Ag_2O \rightarrow Ag + O_2$$

56. Balance the following disproportionation reactions, giving the equations to represent the half-reactions

for each of them:

$$K_2SO_3 \rightarrow K_2SO_4 + K_2S$$

$$K_2MnO_4 + H_2O \rightarrow KMnO_4 + MnO_2 + KOH$$

$$HClO_3 \rightarrow ClO_2 + HClO_4$$

$$HNO_2 \rightarrow HNO_3 + NO + H_2O$$

In what do these reactions differ from intermolecular and intramolecular redox reactions?

2
FUNDAMENTALS OF THE THEORY OF ELECTROLYTIC DISSOCIATION

2.1 ELECTROLYTES AND NONELECTROLYTES. ELECTROLYTIC DISSOCIATION

In terms of ability to conduct electricity, substances are divided into electrolytes and nonelectrolytes.

Substances the solutions of which conduct electricity are called electrolytes.

Solutions of acids, alkalies and salts are examples of electrolytes. Salts and alkalies conduct electricity not only in solution, but in molten state as well.

Substances the solutions of which do not conduct electricity are called nonelectrolytes.

A number of organic compounds such as alcohols, sugar, benzene, certain organic acids fall in this category.

If $CuCl_2$ crystals are thrown into water, the solution will contain positively charged Cu^{2+} ions and negative Cl^- ions. Now if electrodes are inserted into the solution and the circuit is closed, the positive copper ions will move to the negatively charged electrode, while the negative chlorine ions to the positive pole of the battery. Thus electric current will flow through the system.

Decomposition of an electrolyte dissolved in water into ions is called electrolytic dissociation.

The theory of electrolytic dissociation was put forward by the Swedish scientist S.A. Arrhenius in 1887. At present the dissociation of electrolytes is accounted for by the chemical interaction of electrolytes with solvents.

Electrolytic dissociation occurs only in those liquids the molecules of which exhibit strong polar bonding. Water, liquid ammonia, hydrogen peroxide and others are a few examples of such liquids.

In water, an electrolyte molecule is surrounded by water molecules such that their positive ends face the negative end of electrolyte molecule, while the negative ends of water molecules face the positive electrolyte molecule end, thereby attracting each other. This results in weakening of the bond between the ions in an electrolyte molecule and the latter dissociates into ions. The resultant ions are not free, but rather hydrated, i.e. held by water molecules. For example, white anhydrous copper sulphate, on dissolution in water, acquires a blue colour because it is converted into $[Cu(H_2O)_6]^{2+}$ ion. Hydrogen ion (H^+) is converted in a solution to hydroxonium ion (H_3O^+). The number of water molecules held by a given metal ion is determined by the size of the ion. Small ions form tetrahydrates such as $[Be(H_2O)_4]^{2+}$, while larger ions such as Ni^{2+}, Al^{3+} form hexahydrates, $[Ni(H_2O)_6]^{2+}$, $[Al(H_2O)_6]^{3+}$. The number of water molecules held by a given ion is, however, not always known. Moreover, during ionic reactions these water molecules may detach from the ions. This is the reason why in ionic equations the symbol H^+ is used instead of H_3O^+ and Zn^{2+} instead of $[Zn(H_2O)_6]^{2+}$.

Since oppositely charged ions are in a continuous motion, they are attracted to one another according to the Coulomb's law, and electrolyte molecules are formed in a solution. The process of formation of molecules from ions is called *association*. The electrolytic dissociation is, therefore, a reversible process denoted by the sign $\rightleftarrows$. An electrolyte solution should be electroneutral, that is, the number of positive charges should equal the number of negative ones. The positively charged ions are called *cations*, while the negatively charged ones *anions*. An equilibrium state of an aqueous electrolyte solution is characterized by the degree of electrolytic dissociation which is equal to the ratio of the number of dissociated molecules to the total number of dissolved molecules. The degree of dissociation is expressed either in percents or in fractions and denoted by the Greek letter α.

For example, "the degree of dissociation is 80%" means that out of every 100 molecules, 80 dissociate into ions.

In terms of degree of dissociation electrolytes are classified into three groups: strong (for which $\alpha > 30\%$), moderately weak (α ranges from 2 to 30%), and weak ($\alpha < 2\%$) (see Appendix, Table IV).

Using the theory of electrolytic dissociation, Arrhenius gave new definitions to bases, acids and salts.

2.2 DISSOCIATION OF BASES, ACIDS AND SALTS

Strong electrolytes dissociate completely in an aqueous solution (at one step), while weak ones undergo partial dissociation, which takes place in steps.

Bases are electrolytes which dissociate to yield hydroxyl ions, OH^-. For example: $NaOH \rightleftarrows Na^+ + OH^-$.

If a base contains several OH^- groups in its molecule, then the dissociation may take place in steps as shown below:

$$Ba(OH)_2 \rightleftarrows Ba(OH)^+ + OH^- \text{ (first step)}$$
$$Ba(OH)^+ \rightleftarrows Ba^{2+} + OH^- \text{ (second step)}$$

First, one hydroxyl ion is detached. The second hydroxyl ion can be detached only in very dilute solutions. The equation for the complete dissociation may be written as:

$$Ba(OH)_2 \rightleftarrows Ba^{2+} + 2OH^-$$

Acids are electrolytes which dissociate to form hydrogen ions, H^+:

$$HNO_3 \rightleftarrows H^+ + NO_3^-$$

Polybasic weak acids undergo dissociation in steps:

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \text{ (first step)}$$
$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-} \text{ (second step)}$$
$$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-} \text{ (third step)}$$

Salts are of the following types: neutral (also called normal), acid, basic, double, mixed and complex.

Neutral salts, which are soluble in water, are strong electrolytes. These ionize to yield positive metal ions and negative ions of the corresponding acid residue.

A few examples are:

$$Ca(NO_3)_2 \rightleftarrows Ca^{2+} + 2NO_3^-$$

$$Al_2(SO_4)_3 \rightleftarrows 2Al^{3+} + 3SO_4^{2-}$$

Acid salts are electrolytes which contain in the anionic part a hydrogen which can be detached in the form of H^+ ion. These salts are regarded as polybasic acids in which hydrogen atoms are partially replaced by metals. Dissociation of acid salts takes place in steps. For example:

$$Ca(H_2PO_4)_2 \rightleftarrows Ca^{2+} + 2H_2PO_4^- \text{ (first step)}$$

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-} \text{ (second step)}$$

$$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-} \text{ (third step)}$$

But the degree of dissociation in the second step is already very small. This is why an acid salt solution contains only an insignificant number of hydrogen ions.

Basic salts are electrolytes whose cationic part contains one or several hydroxyl groups (OH^-) that can detach in the form of OH^- ions. Basic salts are typical of polyvalent metals. These salts dissociate to give basic and acid residues: $FeOHCl_2 \rightleftarrows FeOH^{2+} + 2Cl^-$.

Dissociation of the basic residue ions into metal ions and a hydroxyl group practically does not take place.

PROBLEMS AND EXERCISES

1. Which substances belong to electrolytes? Give definition of an electrolyte.
2. What do you understand by the degree of dissociation? How is it quantitatively expressed? What does it depend upon?
3. What is termed as electrolytic dissociation? Who is the author of the theory of electrolytic dissociation? What is the conductivity of electrolyte solutions accounted for?
4. What particles are called (a) ions, (b) cations and (c) anions?
5. Which ions are there in aqueous solutions of (a) bases, (b) acids and (c) salts?
6. From the viewpoint of the theory of electrolytic dissociation define bases, acids and salts.

7. What are the differences exhibited by the particles depicted by the following symbols: (a) H, H_2, H^+, (b) S, S^{2-}, SO_2, (c) Cl_2, Cl, Cl^- and (d) K, K^+?

8. Which of the following substances conduct electricity: alcohol, an aqueous nitric acid solution, tap water, molten potassium hydroxide, dry common salt, sulphuric acid containing 100% by mass of H_2SO_4, an aqueous solution of potassium bicarbonate, molten potassium phosphate, an aqueous solution of oxygen, an aqueous sugar solution?

9. What do you understand by strong and weak electrolytes? Illustrate with examples.

10. What conclusions can be drawn regarding the properties of acids, bases and salts on the basis of the theory of electrolytic dissociation?

11. What are hydrated ions?

12. How would you explain different colours of anhydrous copper sulphate and blue vitriol?

13. Explain the similarity in certain properties of acids and alkalies.

14. What common ions are there in the solutions of (a) sulphates, (b) nitrates, (c) carbonates and (d) sulphides? Mention their charges.

15. Write the equations for complete electrolytic dissociation of the following strong electrolytes: H_2SO_4, HNO_3, Na_2SO_4, $Ca(OH)_2$, $Ba(OH)_2$, HCl, NaCl, $AlCl_3$ and $HClO_4$.

16. Write the equations for stepwise dissociation of the following weak and moderately weak electrolytes: H_2CO_3, H_3PO_4, H_2SO_3, H_2S and H_3AsO_3.

17. Write the formulas of salts formed by the following cations and anions: K^+ and NO_3^-, Na^+ and HSO_3^-, Ca^{2+} and HS^-, Mg^{2+} and HSO_4^-, Zn^{2+} and SO_4^{2-}, $[Fe(OH)_2]^+$ and Cl^-, $ZnOH^+$ and NO_3^-, $AlOH^{2+}$ and SO_4^{2-}; Cu^{2+} and HSO_3^-, Al^{3+} and Cl^-.

18. Write the equations for the reactions by which neutral and basic salts are formed when copper or chromium hydroxides react with each of sulphuric and hydrochloric acids.

19. Write the equations for the reactions that occur when sodium, calcium or aluminium hydroxides respectively react with orthophosphoric and carbonic acids to form acid salts.

20. Solutions of certain sodium salts are coloured. What (cations or anions) are responsible for this colour? Illustrate with examples.

21. The aqueous solution of a substance conducts electricity well and does not turn a litmus paper either red or blue. Which class does the substance belong to?

22. Which ions are there in aqueous solutions of barium hydroxide, sulphuric acid, zinc sulphate, potassium bisulphate, hydroxoferrous chloride, hydrobromic acid, strontium hydroxide and cuprous nitrate?

23. Write down the equations for electrolytic dissociation of the following water-soluble substances: $KAl(SO_4)_2$, $Ca(H_2PO_4)_2$, $FeOH(NO_3)_2$, $MgClNO_3$, $KCl \cdot MgCl_2$, $CuSO_4 \cdot 5H_2O$, $KCl \cdot MgSO_4 \cdot 3H_2O$, NH_4KSO_3, $Ba(HCO_3)_2$, $AlOHCl_2$ and $FeSO_4Cl$.

24. Write down the equations to represent the stepwise dissociation of the following electrolytes: $Ba(OH)_2$, H_2SeO_4, $NaHCO_3$, $MgOHNO_3$, H_3AsO_4, KHS, $Ca(OH)_2$ and $Fe(OH)_2NO_3$.

25. How many free ions will be obtained on complete dissociation of each molecule of the following substances: K_2SO_4, $NH_4K_2PO_4$, $NaHSO_3$, $CaOHNO_3$, $CaBr_2$, $Ba(HCO_3)_2$, $KNaSO_4$, MgOHCl and NH_4NO_3? Write down the corresponding equations.

26. Write down the formulas of the substances the aqueous solutions of which contain the following ions:

(a) NO_3^-, HSO_3^-, $MgOH^+$, PO_4^{3-}, OH^-, H^+

(b) S^{2-}, $H_2PO_4^-$, $Fe(OH)^{2+}$, CO_3^{2-}, NH_4^+

27. Write down the equations for electrolytic dissociation of aluminium chloride, ferrous sulphate, potassium bisulphate, sodium sulphate, dihydroxoaluminium nitrate, barium dihydrogen phosphate, sodium carbonate, potassium silicate, hydroxozinc chloride and calcium nitrate.

28. Write down all steps for electrolytic dissociation of the following acids: H_3BO_3, H_2CO_3, H_2S, $H_4P_2O_7$, H_2SO_3 and H_3SbO_4.

2.3 IONIC REACTIONS

When electrolytes react, only the oppositely charged ions are combined. If, as a result of such a reaction a new substance is formed in the form of a precipitate, gas, weak electrolyte or complex ions, then such reactions may be regarded as irreversible, that is, practically going "to completion"*. These are termed as *ionic reactions* and should be written in the form of *ionic equations.*

In ionic equations the precipitate, gas or weakly dissociating compounds are always written in the molecular form. Let us consider the reaction between sodium chloride and silver nitrate to yield silver chloride as one of the products. The molecular equation is as follows:

$$\underset{\substack{\text{strong}\\\text{elec-}\\\text{trolyte}}}{NaCl} + \underset{\substack{\text{strong}\\\text{elec-}\\\text{trolyte}}}{AgNO_3} = \underset{\substack{\text{weak}\\\text{elec-}\\\text{trolyte}}}{AgCl\downarrow} + \underset{\substack{\text{strong}\\\text{elec-}\\\text{trolyte}}}{NaNO_3}$$

Both reactants are ionized in the aqueous solution and exist as Na^+, Cl^-, Ag^+, and NO_3^- ions. The precipitate (AgCl) is formed as a result of reaction between Ag^+ and Cl^- ions. AgCl in this case is a weakly dissociating compound. The net ionic equation looks like:

$$Ag^+ + Cl^- = AgCl\downarrow$$

The overall ionic equation is written as

$$Na^+ + Cl^- + Ag^+ + NO_3^- = AgCl\downarrow + Na^+ + NO_3^-$$

If two strong electrolytes react to afford another two strong electrolytes, then this is a reversible reaction, e.g.:

$$\underset{\substack{\text{strong}\\\text{elec-}\\\text{trolyte}}}{K_2SO_4} + \underset{\substack{\text{strong}\\\text{elec-}\\\text{trolyte}}}{CuCl_2} \rightleftarrows \underset{\substack{\text{strong}\\\text{elec-}\\\text{trolyte}}}{2KCl} + \underset{\substack{\text{strong}\\\text{elec-}\\\text{trolyte}}}{CuSO_4}$$

$$2K^+ + SO_4^{2-} + Cu^{2+} + 2Cl^- \rightleftarrows 2K^+ + 2Cl^- + Cu^{2+} + SO_4^{2-}$$

* According to modern notions of the theory of chemical equilibrium, it is assumed that a reaction between ions in a solution never goes to the end. The final products of such a reaction is nothing but an equilibrium system consisting of molecules and ions. For example, it is wrong to assume that $BaSO_4$ is absolutely insoluble in water, because some Ba^{2+} and SO_4^{2-} ions will remain in the solution. But their amount is small and, hence, may practically be disregarded.

Reactions yielding gases:

$$Na_2S + 2HCl = 2NaCl + H_2S\uparrow$$

For simplicity and convenience let us write the equation for this reaction in the net ionic form: $2H^+ + S^{2-} = H_2S\uparrow$. If one of the reactants is slightly soluble in water (a nonelectrolyte), then this reactant is written in the molecular form as follows:

$$Ca_3P_2 + 6HNO_3 = 3Ca(NO_3)_2 + 2PH_3\uparrow$$
$$Ca_3P_2 + 6H^+ = 3Ca^{2+} + 2PH_3\uparrow$$

Reactions yielding precipitates. Both reactants should be preliminarily dissolved in water, and after the interaction, an insoluble product is formed (see Appendix I). The following example illustrates this case:

$$CuCl_2 + 2KOH = Cu(OH)_2\downarrow + 2KCl$$
$$Cu^{2+} + 2OH^- = Cu(OH)_2\downarrow$$

Reactions leading to weak electrolytes. Weak electrolytes are those which have a degree of dissociation less than 2%. Examples are water, weak acids, slightly soluble bases, salts and so on.

1. $Ca(HCO_3)_2 + 2HBr = CaBr_2 + 2H_2O + 2CO_2\uparrow$
   $HCO_3^- + H^+ = H_2O + CO_2\uparrow$
2. $2CrOHSO_4 + H_2SO_4 = Cr_2(SO_4)_3 + 2H_2O$
   $CrOH^{2+} + H^+ = Cr^{3+} + H_2O$
3. $Al_2O_3 + 2NaOH + 3H_2O = 2Na[Al(OH)_4]$
   $Al_2O_3 + 2OH^- + 3H_2O = 2[Al(OH)_4]^-$
4. A complex ion is formed in a solution:

$$Al(OH)_3 + KOH = K[Al(OH)_4]$$
$$Al(OH)_3 + OH^- = [Al(OH)_4]^-$$

5. Aluminate ion is formed in a melt:

$$Al(OH)_3 + KOH = KAlO_2 + 2H_2O$$
$$Al(OH)_3 + OH^- = AlO_2^- + 2H_2O$$

PROBLEMS AND EXERCISES

1. Write down the ionic equations for the following reactions:

(a) $Na_2S + ZnCl_2 \rightarrow ZnS\downarrow + NaCl$
(b) $Na_2CO_3 + BaCl_2 \rightarrow BaCO_3\downarrow + NaCl$
(c) $K_2CO_3 + CaCl_2 \rightarrow CaCO_3\downarrow + KCl$
(d) $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + NaCl$
(e) $Pb(NO_3)_2 + NaI \rightarrow PbI_2\downarrow + NaNO_3$

2. Write down the ionic equations for the reactions which yield volatile products:

(a) $FeS + HCl \rightarrow H_2S\uparrow + FeCl_2$
(b) $Ca(OH)_2 + NH_4Cl \rightarrow NH_3\uparrow + H_2O + CaCl_2$
(c) $NaCl + H_2SO_4(conc.) \rightarrow HCl\uparrow + Na_2SO_4$

3. Write down the equations for the reactions (in molecular and ionic forms) of (a) hydrochloric acid + silver nitrate, (b) barium chloride + sulphuric acid, (c) sodium hydroxide + ammonium chloride, (d) sodium carbonate + calcium hydroxide, (e) ferric hydroxide + nitric acid.

4. Write down three molecular equations for each of the following ionic equations:

(a) $Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$
(b) $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\downarrow$
(c) $Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3\downarrow$

5. Write down the following equations in complete and net ionic forms:

(a) $Ca(OH)_2 + CO_2 \rightarrow \ldots$
(b) $CuCl_2 + KOH \rightarrow \ldots$
(c) $NH_4OH + HBr \rightarrow \ldots$
(d) $Na_2S + HCl \rightarrow \ldots$

6. Write down the molecular equations for the following ionic equations:

(a) $Fe^{2+} + S^{2-} \rightarrow FeS$
(b) $H^+ + OH^- \rightarrow H_2O$
(c) $Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+} + 3H_2O$
(d) $CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$
(e) $Pb^{2+} + H_2S \rightarrow PbS + 2H^+$
(f) $Mg + 2H^+ \rightarrow Mg^{2+} + H_2$

7. Write down the ionic equations for the following reactions which yield weakly dissociating compounds:

(a) $CH_3COONa + H_2SO_4 \rightarrow \ldots$
(b) $NaCN + H_2SO_4 \rightarrow \ldots$
(c) $Na_2CO_3 + H_2SO_4 \rightarrow \ldots$
(d) $FeS + H_2SO_4 \rightarrow \ldots$

8. Write down the molecular and ionic equations for the reactions of each of hydrochloric acid and sodium hydroxide with each of $Cr(OH)_3$ and $Zn(OH)_2$.

9. Write down the molecular and ionic equations for the following neutralization reactions:

(a) $Al(OH)_3 + HCl \rightarrow \ldots$ (b) $Ca(OH)_2 + H_3PO_4 \rightarrow \ldots$
(c) $KOH + H_2SO_4 \rightarrow \ldots$ (d) $Cu(OH)_2 + HNO_3 \rightarrow \ldots$
(e) $NH_4OH + HCl \rightarrow \ldots$ (f) $Ba(OH)_2 + H_2S \rightarrow \ldots$

10. Write down the molecular and ionic equations for the following reactions which yield neutral salts from basic and acid salts:

(a) $Al(CH)_2Cl + HNO_3 \rightarrow \ldots$ (b) $(MgOH)_2SO_4 + H_2SO_4 \rightarrow \ldots$
(c) $CrOHCl_2 + HCl \rightarrow \ldots$ (d) $KHCO_3 + Ca(OH)_2 \rightarrow \ldots$
(e) $Ca(H_2PO_4)_2 + Ca(OH)_2 \rightarrow \ldots$ (f) $NaHS + NaOH \rightarrow \ldots$

11. Write down the molecular and ionic equations for the reactions going to completion between (a) $Cu(NO_3)_2$ and KOH, (b) $BaCl_2$ and Na_2SO_4; (c) KNO_3 and Na_2SO_3, (d) HNO_3 and HCl, (e) $AgNO_3$ and NaCl.

12. Write down the complete ionic and molecular equations for the reactions that take place in the following cases:

(a) $(AlOH)^{2+} + H^+ \rightarrow Al^{3+} + H_2O$
(b) $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$
(c) $Al(OH)_3 + OH^- \rightarrow AlO_2^- + H_2O$
(d) $Fe(OH)_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O$

13. Explain with the help of ionic equations what will happen on mixing the following ions in solution: (a) Na^+, SO_4^{2-}, SO_3^{2-}, H^+; (b) Al^{3+}, SO_4^{2-}, Cl^-, H^+; (c) Fe^{3+}, OH^-, K^+, NO_3^-; (d) K^+, OH^-, Fe^{3+}, Cl^-; (e) Ca^{2+}, OH^-, Zn^{2+}, PO_4^{3-}.

14. Give examples of three reactions which can be expressed by one ionic equation: $CH_3COO^- + H^+ \rightarrow \rightarrow CH_3COOH$.

15. Is it possible to prepare a solution which would contain the following substances simultaneously: (a) $Mg(OH)_2$ and HNO_3, (b) $Al(OH)_3$ and KOH, (c) H_2SO_4 and NaOH? Confirm your answer with equations.

16. Write the complete ionic and molecular equations for the reactions:

(a) $Ag^+ + Br^- = AgBr$ (b) $Ba^{2+} + SO_4^{2-} = BaSO_4$
(c) $3H^+ + PO_4^{3-} = H_3PO_4$ (d) $2H^+ + SO_3^{2-} = H_2O + SO_2$
(e) $Ba^{2+} + CO_3^{2-} = BaCO_3$

17. Write down the equations for the reactions which proceed on mixing solutions of (a) sulphuric acid and calcium hydroxide, (b) magnesium hydroxide and hydrochloric acid, (c) zinc hydroxide and potassium hydroxide.

2.4 CONCENTRATION OF SOLUTIONS

The concentrations of solutions can be expressed in a number of ways: mass fraction of a solute (or mass percent), molar concentration (molarity), normal concentration (normality) and others.

The mass fraction of a solute, w, is the ratio of the mass of the solute to the total mass of the solution. That is,

$$w = \frac{m}{m_1}$$

where w is the mass fraction of the solute, m the mass of the solute and m_1 the total mass of the solution containing the solute. Mass fractions are generally expressed either as fractions of unity or in percents. Mass percent, $w = (m/m_1) \times 100\%$. For example, "mass fraction of KOH in water equals 0.4 (or 40%)" means that in such a KOH solution there are 40 units by mass of KOH per every 100 units by mass of the solution. Mass percent is also called percent strength.

Example 1. Determine the mass percent of KOH in a solution containing 40 g of KOH in 160 g of water.

Solution. Here, the total mass of the KOH solution, $m_1 = 160 + 40 = 200$ g.

Substituting the known values of m and m_1 in the formula for mass percent, we get

$$w = (m/m_1) \times 100\% = (40 \text{ g}/200 \text{ g}) \times 100\% = 20\%$$

Example 2. 120 g of a solution containing 40% by mass of NaCl are mixed with 200 g of a solution containing 15% by mass of NaCl. Determine the mass percent of sodium chloride in the final solution.

Solution. Let us first determine the amount of sodium chloride in 120 g of a solution containing 40% by mass of NaCl:

$$m = \frac{wm_1}{100\%} = \frac{40\% \times 120 \text{ g}}{100\%} = 48 \text{ g}$$

Likewise, the amount of sodium chloride in 200 g of a solution containing 15% by mass of NaCl is:

$$m = \frac{15\% \times 200 \text{ g}}{100\%} = 30 \text{ g}$$

Now, the total mass of the solution is 120 g + 200 g = = 320 g and that of the solute (NaCl) is 48 g + 30 g = = 78 g. The mass percent of sodium chloride in the final solution is, therefore, equal to $w = (78 \text{ g}/320 \text{ g}) \times 100\% = 24.4\%$.

The molar concentration (molarity) denoted by c_M shows the number of moles of a solute per litre of a solution.

Molarity is the ratio of the amount of a solute (m/M) to the volume of its solution (V), that is, $c_M = m/(MV)$ mole/litre, where m is the mass of the solute in g, M is the molar mass of the solute in g/mole and V is the volume of the solution in litre.

If 1 litre of a solution contains 1 mole of a solute, the solution is termed as unimolar and denoted by 1 M. A solution containing 2 moles of a solute per litre of a solution is called a bimolar solution and denoted by 2 M, 0.1 mole of a solute per litre of a solution decimolar (0.1 M) and so on. Thus, a unimolar H_2SO_4 solution is such a solution 1 litre of which contains 1 mole or 98 g of H_2SO_4.

Example 3. How many grams of NaOH are there in 500 ml of 0.1 *M* solution?

Solution. Method 1.

$$m(\text{NaOH}) = \frac{c_M MV}{1000} = \frac{0.1 \text{ mole} \times 40 \text{ (g/mole)} \times 500 \text{ ml}}{1000 \text{ ml}} = 2 \text{ g}$$

Method 2.

1 *M* NaOH solution contains 40 g of NaOH

0.1 *M* NaOH solution contains, say, *X* g of NaOH

$$X = \frac{40 \text{ g} \times 0.1 M}{1 M} = 4 \text{ g}$$

1000 ml of 0.1 *M* NaOH solution contain 4 g of NaOH

500 ml of 0.1 *M* NaOH solution contain, say, *Y* g of NaOH

$$Y = \frac{4 \text{ g} \times 500 \text{ ml}}{1000 \text{ ml}} = 2 \text{ g}$$

Example 4. Calculate the molarity of an NaOH solution 500 ml of which contain 1 g of NaOH.

Solution. Method 1.

$$c_M = \frac{1000 \text{ ml} \times 1 \text{ g}}{40 \text{ (g/mole)} \times 500 \text{ ml}} = 0.05 \text{ mole/litre or } 0.05 M$$

Method 2.

500 ml of NaOH solution contain 1 g of NaOH

1000 ml of NaOH solution contain, say, *X* g of NaOH

$$X = \frac{1000 \text{ ml} \times 1 \text{ g}}{500 \text{ ml}} = 2 \text{ g}$$

Now we can find the concentration in the following way:

1000 ml of 1 *M* NaOH solution contain 40 g of NaOH

1000 ml of *Y M* NaOH solution contain 2 g of NaOH

$$Y = \frac{1 M \times 2 \text{ g}}{40 \text{ g}} = 0.05 M$$

To prepare solutions of a given molarity, a special measuring glassware is used which is called a measuring flask with a long narrow neck containing a ring-shaped mark around it.

Say, we need prepare 500 ml of a molar NaOH solution. For this purpose, we should first calculate the mass of

NaOH in this solution:

1000 ml of 1 *M* NaOH solution contain 40 g of NaOH
500 ml of 1 *M* NaOH solution contain *X* g of NaOH

$$X = \frac{40 \text{ g} \times 500 \text{ ml}}{1000 \text{ ml}} = 20 \text{ g}$$

Now we place 20 g of NaOH in a 500-ml measuring flask and add a small volume of water to it to fully dissolve the NaOH sample. When the whole NaOH has been dissolved, we add water to the mark of the flask (the lower edge of the meniscus should touch the mark). After stoppering the flask, we shake the solution. 1 *M* NaOH solution is thus ready for use.

Generally, in the laboratories molar solutions are prepared. Such solutions always contain a strictly fixed number of molecules. For example, 1 litre of a molar solution of any substance contains 6.02×10^{23} molecules.

PROBLEMS AND EXERCISES

1. Determine the mass percent of NaCl in a solution prepared by dissolving 20 g of NaCl in 300 ml of water.

2. How many grams of potassium hydroxide are there in 200 ml of 10% KOH solution having a density of 1.09 g/ml?

3. How many grams of sodium hydroxide are there in 250 g of 20% NaOH solution?

4. A mass of 40 g of KOH was added to 300 ml of 20% KOH solution which has a density of 1.2 g/ml. Determine the mass percent of KOH in the obtained solution.

5. One litre of water was poured into 200 ml of 10% H_2SO_4 solution of density 1.066 g/ml. Determine the mass percent of H_2SO_4 in the solution thus obtained.

6. Determine the mass percent of sodium chloride in a solution prepared by mixing 200 g of 20% NaCl solution with 100 ml of 30% NaCl solution which has a density of 1.15 g/ml.

7. A mass of 150 g of a solution is obtained by evaporating 500 g of 1% NaCl solution. What is the percent strength of the new solution?

8. How many millilitres of nitric acid containing 20 mass percent of HNO_3 and having a density of 1.115 g/ml will be required to neutralize a solution containing 5.6 g of KOH?

9*. 4.6 g of metallic sodium were treated with 200 ml of water. Determine the mass percent of the alkali thus formed.

10*. Calculate the mass percent of sulphuric acid in a solution prepared by dissolving 4 g of sulphur trioxide in a sulphuric acid solution containing 80 mass percent of H_2SO_4 and having a density of 1.73 g/ml.

11. What volume of hydrochloric acid containing 20% by mass of HCl and having a density of 1.1 g/ml is required to dissolve 200 g of limestone containing 85% calcium carbonate? What volume will occupy at STP the gas which will evolve as a result of this dissolution?

12. How much water is to be added to 3 kg of a 20% solution to convert it to a 15% solution?

13. How much salt is to be dissolved in 2 kg of water to get a 20% solution?

14. How many millilitres of sulphuric acid solution which contains 60 mass percent of H_2SO_4 and has a density of 1.5 g/ml are to be taken to prepare 2.5 litres of a solution which would have 12 mass percent of H_2SO_4 and a density of 1.08 g/ml?

15. A mass of 25 g of a mixture of zinc and zinc oxide was treated with 40% potassium hydroxide solution which has a density of 1.39 g/ml. This resulted in evolution of 4.48 litres (at STP) of a gas. How many millilitres of alkali were used for this purpose?

16*. A mass of 9.2 g of a mixture of aluminium and zinc was treated with a sodium hydroxide solution containing 48% by mass of NaOH and having a density of 1.5 g/ml. This effected the evolution of 5.6 litres of a gas measured at STP. How many millilitres of the alkali solution were required to dissolve aluminium?

17. Determine the molar concentration of an H_3PO_4 solution, 500 ml of which contain 9.8 g of H_3PO_4.

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* Problems with a greater level of sophistication are marked with an asterisk—*Tr.*

18. How many grams of Na_2CO_3 are there in 200 ml of 0.1 *M* solution?

19. How many millilitres of concentrated sulphuric acid of density 1.84 g/ml and containing 98% by mass of H_2SO_4 are to be taken to prepare 500 ml of 3 *M* solution?

20. How to get a volume of 500 ml of 0.25 *M* solution from 1.5 *M* $Ca(OH)_2$ solution?

21. How many millilitres of calcium nitrate solution which contains 70% by mass of $Ca(NO_3)_2$ and has a density of 1.5 g/ml are to be taken to prepare 250 ml of 0.1 *M* solution?

22. 12 ml of a sulphuric acid solution are required for a reaction with 0.44 g of sodium carbonate. Calculate the molarity of the sulphuric acid solution.

23*. A volume of 1 litre of a potassium hydroxide solution which contains 10% by mass of KOH and has a density of 1.05 g/ml was mixed with a volume of 0.5 litre of a hydrochloric acid solution containing 10 mass % HCl and having a density of 1.05 g/ml. Determine the mass percent of the salt in the obtained solution.

24*. Sodium chloride reacted under mild heating with 40% sulphuric acid solution of density 1.4 g/ml to evolve 5.6 litres of hydrogen chloride measured at STP. This hydrogen chloride was then dissolved in 20 ml of water. How many millilitres of sulphuric acid entered the reaction? What is the percent strength of the hydrochloric acid thus formed?

25. An excess of barium chloride was added to 200 ml of sulphuric acid solution. The mass of the separated precipitate after washing and drying was found to be 1.165 g. What is the molar concentration of the sulphuric acid solution employed?

26*. How many millilitres of 8% sodium hydroxide solution, which has a density of 1.09 g/ml, will be required to neutralize 100 ml of sulphuric acid solution, if it is known that when an excess of barium chloride is added to 10 ml of the given sulphuric acid solution, a mass of 0.233 g of barium sulphate is formed?

27*. 8 litres of sulphuric acid containing 40% by mass of H_2SO_4 and having a density of 1.3 g/ml were evaporated to 5200 g. Determine the mass percent of sulphuric

acid in the final solution. How many grams of 20% sodium hydroxide solution will be required to completely neutralize the resultant H_2SO_4 solution?

28*. To neutralize 10 ml of a sulphuric acid solution, 18 ml of 0.1 *M* potassium hydroxide solution were added. It was found then that the alkali was taken in excess amount. To achieve a neutral reaction, 4 ml of 0.2 *M* hydrochloric acid solution were added. What was the molar concentration of the initial sulphuric acid solution?

29. How much salt is to be added to 350 g of water to obtain 30% salt solution?

30. Determine the mass percent of water of crystallization in blue vitriol, $CuSO_4 \cdot 5H_2O$.

31. 50 g of blue vitriol, $CuSO_4 \cdot 5H_2O$, were dissolved in 350 g of water. What is the mass percent of $CuSO_4$ in the solution thus obtained?

32. Determine the masses of the crystal hydrate $CaCl_2 \cdot 6H_2O$ and water required to prepare 500 ml of a calcium chloride solution containing 40% by mass of $CaCl_2$ and having a density of 1.4 g/ml.

33. How many grams of crystal hydrate $Na_2SO_4 \times \times 10H_2O$ will be obtained on slow evaporation of water from 500 g of 10% sodium sulphate solution?

34. How many grams of sodium sulphate are to be dissolved in 400 g of water to prepare a solution containing 8% by mass of Na_2SO_4?

35. To prepare a solution with 5% by mass of potassium nitrate, how many grams of the salt are to be dissolved in 150 g of water?

36. How much magnesium chloride is there in 800 ml of a solution with 10% by mass of $MgCl_2$ and a density of 1.06 g/ml?

37. Determine the mass percent of water in sulphuric acid solutions with densities of 1.64, 1.71 and 1.84 g/ml.

38. How many millilitres of a nitric acid solution, which contains 50% by mass of HNO_3 and has a density of 1.32 g/ml, are to be taken for the preparation of 5 litres of a solution containing 2% by mass of HNO_3 and having a density of 1.01 g/ml?

39. How many millilitres of water are to be added to 200 ml of a sodium hydroxide solution which contains

10% by mass of NaOH and has a density of 1.10 g/ml for the preparation of 5% NaOH solution?

40. How many litres of 15% sodium hydroxide solution (density 1.16 g/ml) may be prepared from 2 litres of 33% NaOH solution (density 1.36 g/ml)?

41. Calculate the mass of the precipitate formed when 10 ml of a barium chloride solution containing 12.8% by mass of $BaCl_2$ are added to a sodium sulphate solution.

42. How many litres of 10% sulphuric acid solution with a density of 1.07 g/ml are required to neutralize a mass of 16 kg of sodium hydroxide?

43. What is the mass of nitric acid which is present in 0.4 litre of a solution with $c\ (HNO_3) = 0.1$ mole/litre?

44. A volume of 0.5 litre of a solution contains 14 g of potassium hydroxide. What is the molar concentration of this solution?

45. 0.75 litre of a solution contains 4.4 g of sodium chloride. What is the molar concentration of the solution?

46. What is the volume of 0.1 *M* solution of sulphuric acid which contains 4.9 g of H_2SO_4?

47. Determine the molar concentration of 8% sodium hydroxide solution which has a density of 1.09 g/ml.

48. Calculate the mass percent of NaOH in 2 *M* sodium hydroxide solution which has a density of 1.1 g/ml.

49. Calculate the mass of hydrochloric acid contained in 0.25 litre of a solution for which $c\ (HCl) = 1$ mole/litre.

50. Determine the molar concentration of 38% hydrochloric acid solution (density 1.19 g/ml).

51. To prepare 0.2 *M* solution, how much water is to be added to a volume of 200 ml of 0.5 *M* H_2SO_4 solution?

52. Calculate the molar concentration of a solution prepared by diluting 200 ml of 2 *M* solution with 300 ml of water.

53. Calculate the molar concentration of 40% nitric acid solution which has a density of 1.25 g/ml.

54. Determine the molar concentration of a solution prepared by mixing 200 ml of 0.5 *M* sodium nitrate solution with 400 ml of 0.2 *M* solution.

55. Determine the molar concentration of sulphuric acid, if 200 ml of the solution contain 4.9 g of H_2SO_4.

2.5 HYDROLYSIS OF SALTS

Hydrolysis of a salt is an exchange reaction between salt ions and water ions.

During hydrolysis, the equilibrium of the dissociation of water is shifted, for one of the ions (H^+ or OH^-) is bonded into a weak electrolyte. If H^+ ions are bonded then OH^- ions are accumulated in the solution making the latter thereby alkaline. If, on the contrary, OH^- ions are bonded, then an acidic solution results due to accumulation of H^+ ions.

Four cases are to be considered when a salt is dissolved in water, by making use of the concepts of "weak" and "strong" electrolytes.

1. Salt formed by a strong base and a strong acid. In this case neither cations nor anions are hydrolyzed. For example, when potassium nitrate is dissolved in water in the presence of litmus indicator, the latter does not change its colour. The equations for this reaction in the molecular and ionic forms may be represented as follows:

$$KNO_3 + H_2O \rightleftharpoons KOH + HNO_3$$

$$K^+ + NO_3^- + HOH \rightleftharpoons K^+ + OH^- + H^+ + NO_3^-$$

The solution is neutral, because neither H^+ nor OH^- ions form bond with other ions to yield a weak electrolyte.

2. Salt formed by a strong base and a weak acid. Here anions are hydrolyzed. Hydrolysis of CH_3COOK may serve as an example in this case. On dissociation, the salt ions CH_3COO^- and K^+ react with the ions H^+ and OH^- of water. The acetate ions, CH_3COO^-, are bonded by H^+ to afford acetic acid, CH_3COOH, which is a weak electrolyte, while OH^- ions are accumulated in the solution making it alkaline, since K^+ ions cannot form weak electrolyte with OH^- ions (KOH is a strong electrolyte). The equations for the hydrolysis of CH_3COOK will look as below:

molecular form

$$CH_3COOK + H_2O \rightleftharpoons KOH + CH_3COOH$$

ionic form

$$K^+ + CH_3COO^- + HOH \rightleftharpoons K^+ + OH^- + CH_3COOH$$

net ionic form

$$CH_3COO^- + HOH \rightleftharpoons OH^- + CH_3COOH$$

While writing the hydrolysis equation, one may start with the net ionic equation and then write a molecular one, avoiding the complete ionic equation.

The hydrolysis of Na_2S takes place stepwise. This salt is formed by a strong base and a weak acid. The cation of the salt will, therefore, form a strong electrolyte NaOH with the OH^- ions of water. This strong electrolyte ionizes nearly completely. The ion Na^+ of this electrolyte is, therefore, excluded from the ionic equations. Then the ionic equation for the first step of the hydrolysis is:

$$S^{2-} + HOH \rightleftharpoons HS^- + OH^- \text{ (the solution is alkaline)}$$

To write the molecular equation, one should bring back the previously excluded Na^+ ion:

$$Na_2S + H_2O \rightleftharpoons NaHS + NaOH$$

The net ionic form for the second step of the hydrolysis of NaHS is as follows:

$$HS^- + HOH \rightleftharpoons H_2S + OH^-$$

while the molecular form is:

$$NaHS + H_2O \rightleftharpoons NaOH + H_2S$$

The second step of this hydrolysis does not practically occur, since the accumulated OH^- ions make the solution strongly alkaline. This results in neutralization and in a shift of the equilibrium to the left.

3. Salt formed by a weak base and a strong acid. The cations are hydrolyzed this time. An example is the hydrolysis of NH_4Cl salt formed from NH_4OH, a weak base, and HCl, a strong acid. The Cl^- ion is to be discarded here, since with the cation of water it forms a strong electrolyte. Then the hydrolysis equation in the net

ionic form will look as below:

$$NH_4^+ + HOH \rightleftharpoons NH_4OH + H^+$$

and in the molecular form:

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

In this case the OH^- ions are bonded into a weak electrolyte, while the H^+ ions are accumulated in the solution. The solution is, therefore, acidic in nature.

Let us consider another example: hydrolysis of $Zn(NO_3)_2$ which hydrolyzes in steps. After discarding the NO_3^- ion of the strong electrolyte, one can write the net ionic equation for the first step:

$$Zn^{2+} + HOH \rightleftharpoons ZnOH^+ + H^+$$

that is, the OH^- ions become bonded, while the H^+ ions are accumulated.

To write the hydrolysis equation in the molecular form, the discarded ion, that is, NO_3^- is to be added:

$$Zn(NO_3)_2 + H_2O \rightleftharpoons ZnOHNO_3 + HNO_3$$

The second step of this hydrolysis has the following net ionic equation:

$$ZnOH^+ + HOH \rightleftharpoons Zn(OH)_2 + H^+$$

while the corresponding molecular equation looks as below:

$$ZnOHNO_3 + H_2O \rightleftharpoons Zn(OH)_2 + HNO_3$$

The second step of this hydrolysis does not practically take place, since the solution turns strongly acidic as a result of accumulation of H^+ ions and zinc hydroxide is dissolved.

4. Salt formed by a weak base and a weak acid. Both the cations and anions are hydrolyzed here. This may be illustrated by the hydrolysis of CH_3COONH_4. Let us first write the equation in the ionic form:

$$NH_4^+ + CH_3COO^- + HOH \rightleftharpoons NH_4OH + CH_3COOH$$

A weak base and a weak acid are formed. The degrees of dissociation of these two are nearly the same. Therefore, on hydrolysis, the solution will be nearly neutral.

Let us consider another example. Hydrolysis of Al_2S_3 goes to completion and this is an irreversible process.

The reason for this is that this reaction leads to a precipitate and evolution of a gas:

$$Al_2S_3 + 6H_2O \rightarrow 3H_2S\uparrow + 2Al(OH)_3\downarrow$$
$$2Al^{3+} + 3S^{2-} + 6HOH = 3H_2S\uparrow + 2Al(OH)_3\downarrow$$

Now we discuss the factors influencing hydrolysis. Hydrolysis is generally accelerated with dilution of salt solutions. This is accounted for by the fact that salt molecules dissociate to a greater extent and more particles of a weak electrolyte are formed.

Heating also enhances hydrolysis, since water dissociation increases. For example, hydrolysis of $Fe(CH_3COO)_3$ in the cold affords $FeOH(CH_3COO)_2$, while $Fe(OH)_2CH_3COO$ precipitates on boiling.

Hydrolysis of two salts may be mutually increased by making their solutions interact. For example, in the solutions of $Fe_2(SO_4)_3$ and K_2CO_3 the following equilibria are established:

$$Fe^{3+} + HOH \rightleftarrows (FeOH)^{2+} + H^+$$
$$CO_3^{2-} + HOH \rightleftarrows (HCO_3)^- + OH^-$$

If these two solutions are mixed, then H^+ and OH^- ions leave the reaction site in the form of water, activating thereby the subsequent hydrolysis steps and yielding finally a base and an acid:

$$Fe_2(SO_4)_3 + 3K_2CO_3 + 3H_2O \rightarrow 2Fe(OH)_3\downarrow + 3CO_2\uparrow + 3K_2SO_4$$

PROBLEMS AND EXERCISES

1. What is termed as hydrolysis? Give examples of salts that are hydrolyzed and of those which are not hydrolyzed. Explain why.
2. How does hydrolysis occur when a salt is made up of: (a) a strong acid and a weak base, (b) a strong base and a weak acid, (c) a weak base and a weak acid?
3. Why does an aluminium nitrate solution turn red when litmus is added?
4. Why does a solution of potassium sulphide become crimson on addition of phenolphthalein?
5. Why do solutions of barium chloride and ammonium carbonate not change the colour of litmus or phenolphthalein?
6. Why is sulphurous acid not formed when sodium

sulphite is hydrolyzed? Why is aluminium hydroxide not precipitated on hydrolysis of aluminium sulphate?

7. Predict whether the following salts will give acidic, basic or neutral solutions when dissolved in water: $(NH_4)_2CO_3$, $(NH_4)_2SO_4$, NH_4NO_2, CH_3COONH_4, KNO_3, $KAl(SO_4)_2$, K_2CO_3, and KH_2PO_4.

8. Of the following salts which will be completely hydrolyzed in aqueous solutions: KCN, CH_3COONa, $(NH_4)_2SO_3$, and BaS?

9. Which salts are partially hydrolyzed? Give examples.

10. Why are salts of strong acids and strong bases not hydrolyzed?

11. What are the factors which influence the hydrolysis of salts? Explain with examples.

12. Explain how the temperature and concentration of a solution influence the hydrolysis of a salt.

13. Predict whether the following salts will give acidic, basic or neutral solutions when dissolved in water: $AlCl_3$, KNO_3, $CuSO_4$, Na_2CO_3, and $(NH_4)_2S$. Write the complete and net ionic equations for the hydrolysis of these salts.

14. Which of the following salts are hydrolyzed: $BaCl_2$, $Pb(NO_3)_2$, K_3PO_4, Na_2CO_3, and $ZnBr_2$? Write the hydrolysis equations in the ionic form where possible.

15. Mention whether the following salts are hydrolyzed in aqueous solutions or not: $NaNO_3$, MgS, CuI_2 and $(NH_4)_2CO_3$. Write the equations in molecular and ionic forms where they are applicable.

16. Write the first steps of the hydrolysis equations in molecular and ionic forms for the following salts: $CuSO_4$, K_2SO_3, $(CH_3COO)_2Ba$, $(NH_4)_3PO_4$, $Fe(OH)_2NO_3$, $AlOHCl_2$, Na_2HPO_4.

17. Predict whether the following salts will result in acidic, basic or neutral aqueous solutions: $AlCl_3$, KNO_2, $CuSO_4$, Na_2SO_3 and $(NH_4)_2S$. Give the respective hydrolysis reactions to support your answer.

18. Write all the three steps for the hydrolysis of $CrCl_3$ in molecular and ionic forms. Name all salts formed in the three steps.

19. Write the molecular and ionic equations for all steps in the hydrolysis of Na_3PO_4. Name all salts formed in these steps.

20. Explain why a solution of K_3PO_4 is strongly alkaline, whereas a solution of KH_2PO_4 weakly acidic.

21. Write the molecular and ionic equations for all steps in the hydrolysis of each of the following basic salts: $BiOH(NO_3)_2$, $(CuOH)_2SO_4$, FeOHCl and $Fe(OH)_2NO_3$. Name all salts formed in different steps.

22. Write the molecular and ionic equations for all steps in the hydrolysis of each of the following acid salts: K_2HPO_4, NH_4HCO_3, $Ba(HS)_2$ and $Ca(HSO_3)_2$. Name all salts formed in these steps.

23*. Indicate how aqueous solutions of the following salts will respond to an indicator: $NH_4Al(SO_4)_2 \cdot 12H_2O$, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$ and $Na_2CO_3 \times \times 10H_2O$. Write the hydrolysis equations in the ionic form.

24. Write the hydrolysis equations for salts, the solutions of which are practically neutral: $(NH_4)_2CO_3$, MgS, $AgNO_3$ and $Cr_2(SO_4)_3$.

25. How is Cr_2S_3 hydrolyzed, if it is known that trivalent metal sulphides undergo complete and irreversible hydrolysis?

26. On mixing $AgNO_3$ and K_2CO_3 solutions, a gas is liberated and Ag_2O is precipitated. Write the respective equations for these reactions.

27. On mixing a $Cr_2(SO_4)_3$ and an Na_2S solutions, $Cr(OH)_3$ is precipitated. Write the respective equations for these reactions in molecular and ionic forms.

28. Write the molecular and ionic equations for the reactions which take place when the solutions of each pair of the following salts are mixed together, assuming the hydrolysis to go to completion: $Al_2(SO_4)_3$ and Na_2CO_3, $Fe(NO_3)_3$ and K_2S, $CrCl_3$ and K_2CO_3.

29. Which of the following salts are hydrolyzed: potassium chloride, potassium sulphite, zinc chloride, calcium nitrate and calcium nitrite?

30. Why aluminium or chromium(III) sulphide cannot be obtained by mixing together solutions of the respective metal nonsulphide salt and an alkali metal sulphide?

31. What will be the colour of litmus in an aqueous solution of each of $CuSO_4$, K_2CO_3, CaS, $NaNO_3$, K_2S, $ZnCl_2$ and NaCN?

32. Write the hydrolysis equations in molecular and ionic forms for each of the following salts: $Fe_2(SO_4)_3$, $FeCl_3$, $Zn(NO_3)_2$, $ZnSO_4$, NH_4Cl and $MgSO_4$. Indicate how hydrolysis may be enhanced or weakened in each of these cases.

33. Select one of the following three cases in which all salts are hydrolyzed: (a) $MgCl_2$, Na_3PO_4 and K_2SO_3; (b) $Mg(NO_3)_2$, $Ba(NO_3)_2$ and NaCl; (c) KBr, K_2S and $Cu(NO_3)_2$.

34. Write two molecular equations for the hydrolysis represented by the following ionic equations:

(a) $Cr^{3+} + H_2O \rightleftarrows (CrOH)^{2+} + H^+$

(b) $S^{2-} + H_2O \rightleftarrows (HS)^- + OH^-$

2.6 ELECTROLYSIS

Oxidation-reduction processes that take place at the electrodes under the action of direct electric current are called electrolysis.

Reactions that occur at the cathode are known as reduction, while those at the anode are oxidation. This may be illustrated by the following example. If direct electric current is passed through molten KI, then K^+ ions arrive at the cathode to take up electrons from it, while I^- ions give up their electrons to the anode. In this way, metallic potassium is formed at the cathode nd iodine at the anode:

$$KI \rightleftarrows K^+ + I^-$$

at cathode: $K^+ + e^- = K$; at anode: $2I^- - 2e^- = I_2$.

During the electrolysis of aqueous electrolytic solutions redox processes become complicated due to the ions formed from water which also take part in the electrolysis. Let us first deal with a few aspects of the processes taking place at the cathode during electrolysis in aqueous solutions.

The higher a metal's position in the series of standard reduction electrode potentials (also called the electrochemical series), the more difficult its ions are reduc d at the cathode (see p. 156).

1. Cations, placed in the series of standard reduction electrode potentials, starting with lithium and ending

with aluminium, i.e., Li^+, K^+, Ca^{2+}, Na^+, Mg^{2+} and Al^{3+} are not reduced during electrolysis of aqueous solutions. Hydrogen gas from water is evolved at the cathode instead. This situation may be illustrated by the electrolysis of a KI solution:

$$KI \rightleftharpoons K^+ + I^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

cathode: K^+, H^+ → anode: I^-, OH^-

$$2H_2O + 2e^- \longrightarrow H_2\uparrow + 2OH^- \qquad 2I^- - 2e^- \longrightarrow I_2\downarrow$$

$$K^+ + OH^- \rightleftharpoons KOH$$

In this way, hydrogen is evolved at the cathode and iodine is formed at the anode, while K^+ ion from KI by combining with OH^- from water gives KOH solution near the cathode:

$$2KI + 2H_2O \rightarrow 2KOH + H_2\uparrow + I_2\downarrow$$

or in the ionic form: $2I^- + 2H_2O \rightarrow 2OH^- + H_2\uparrow + I_2\uparrow$ (the anode processes are not considered here).

2. Cations, arranged in the series of standard reduction electrode potentials, starting with manganese and ending with hydrogen that is, Mn^{2+}, Zn^{2+}, Cr^{3+}, Fe^{2+}, Ni^{2+}, Sn^{2+}, Pb^{2+} and H^+ are reduced along with the water molecules during the electrolysis of solutions. Electrolysis of a $FeSO_4$ solution may serve as an example:

$$FeSO_4 \rightleftharpoons Fe^{2+} + SO_4^{2-}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

cathode: Fe^{2+}, H^+ → anode: SO_4^{2-}, OH^-

$$Fe^{2+} + 2e^- \longrightarrow Fe^0 \qquad 2H_2O - 4e^- \longrightarrow O_2\uparrow + 4H^+$$

$$2H_2O + 2e^- \longrightarrow H_2\uparrow + 2OH^-$$

3. Cations lined in the series of standard reduction electrode potentials after H^+, namely, Cu^{2+}, Hg_2^{2+}, Ag^+, Pt^{2+} and Au^{3+} are practically completely reduced at the cathode. Electrolysis of a $CuCl_2$ solution may be cited as an example:

$$CuCl_2 \rightleftharpoons Cu^{2+} + 2Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

cathode $\boxed{\begin{matrix} Cu^{2+} \\ H^+ \end{matrix}} \rightarrow$ anode $\boxed{\begin{matrix} Cl^- \\ OH^- \end{matrix}} \rightarrow$

$$Cu^{2+} + 2e^- \longrightarrow Cu^0 \qquad 2Cl^- - 2e^- \longrightarrow Cl_2$$

Now let us consider the processes that take place at the anodes. Anions of hydracids and of salts of these acids (F^-, Cl^-, Br^-, I^-, S^{2-}, CN^-, and so on) hold their electrons less tightly than does the OH^- ion from water. This is the reason why during the electrolysis of aqueous solutions of salts of hydracids the acid anions are oxidized. This may be illustrated by the electrolysis of a $BaCl_2$ solution:

$$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

cathode $\boxed{\begin{matrix} Ba^{2+} \\ H^+ \end{matrix}} \rightarrow$ anode $\boxed{\begin{matrix} Cl^- \\ OH^- \end{matrix}} \rightarrow$

$$2H_2O + 2e^- \longrightarrow H_2\uparrow + 2OH^- \qquad 2Cl^- - 2e^- \longrightarrow Cl_2\uparrow$$

Anions of oxyacids (NO_3^-, SO_3^{2-}, CO_4^{2-}, PO_4^{3-}) hold their electrons more tightly than the OH^- ions. Hence during the electrolysis of aqueous solutions of salts of oxyacids water molecule is oxidized: $2H_2O - 4e^- = O_2 + 4H^+$, while the salt ions (anions) remain unchanged. An exam-

ple is the electrolysis of an $Hg(NO_3)_2$ solution:

$$Hg(NO_3)_2 \rightleftharpoons Hg^{2+} + 2NO_3^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

cathode: Hg^{2+}, H^+ → $Hg^{2+} + 2e^- \longrightarrow Hg^0$

anode: NO_3^-, OH^- → $2H_2O - 4e^- \longrightarrow O_2 + 4H^+$

$$H^+ + NO_3^- \rightleftharpoons HNO_3$$

Thus, electrolysis of an $Hg(NO_3)_2$ solution results in the formation of mercury at the cathode and in the evolution of oxygen at the anode, nitric acid being accumulated near the anode. The overall reaction may be represented in the molecular form:

$$2Hg(NO_3)_2 + 2H_2O = 2Hg + O_2 + 4HNO_3$$

or in the ionic form:

$$2Hg^{2+} + 2H_2O = 2Hg + O_2 + 4H^+$$

In the cases discussed above, insoluble anodes are used, which are made up of carbon, graphite, platinum or iridium.

If soluble anodes such as Cu, Ag, Zn, Cd, Hg, Ni and others are employed during electrolysis of an aqueous solution, then the anode itself is oxidized. For example, if for the electrolysis of an aqueous solution of $CuCl_2$ a copper anode is used, then chlorine ions are not oxidized, the anode is dissolved instead:

$$CuCl_2 \rightleftharpoons Cu^{2+} + 2Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

cathode: Cu^{2+}, H^+ → $Cu^{2+} + 2e^- \longrightarrow Cu$

anode (Cu): Cl^-, OH^- → $Cu - 2e^- \longrightarrow Cu^{2+}$

Here copper travels from the anode to the cathode. The quantity of copper chloride in the solution remains unchanged. Electrolysis with soluble anodes finds wide applications in the manufacture of extra-pure metals (the so-called electrolytic refining), in coating one metal by a layer of another (electroplating) and in obtaining images in relief (electroforming).

PROBLEMS AND EXERCISES

1. What is termed as electrolysis?
2. In which cases during electrolysis of aqueous salt solutions (a) hydrogen is evolved at the cathode, (b) oxygen is liberated at the anode and (c) the composition of the electrolyte remains unchanged?
3. Electrolysis of aqueous solutions of which salts results in the reduction at the cathode of (a) metal ions, (b) both metal ions and hydrogen ions from water?
4. Will there be any change in the amount of salt in a solution containing $Cu(NO_3)_2$, Na_2CO_3 or KCl, if the solution is subjected to electrolysis using an insoluble anode?
5. Will the amount of the following salts in their solutions change during electrolysis with a soluble nickel anode: $CaCl_2$, $NiSO_4$ and $Fe(NO_3)_2$?
6. What is formed in the solution near a cathode as a result of electrolysis of aqueous solutions of barium salts?
7. What is formed at the cathode on electrolysis of solutions of sodium salts, if the anode is made up of copper?
8. What is formed in the solution near the anode as a result of electrolysis of an aqueous solution of nickel(II) sulphate, if the anode is made up of (a) carbon and (b) nickel?
9. What is evolved at an insoluble anode on electrolysis of a sulphuric acid solution?
10. What is evolved at an insoluble anode on electrolysis of a potassium chloride solution?
11. What processes occur at the cathode and at a carbon anode as a result of electrolysis of aqueous solutions of (a) $NaNO_3$, (b) $ZnBr_2$ and (c) $HgSO_4$?

12. Will there be any change in the concentration during electrolysis of a sulphuric acid solution?

13. Will there be any change in the concentration of a barium hydroxide solution and in the quantity of barium hydroxide during electrolysis?

14. In which order will the following cations be reduced as a result of electrolysis of their mixture having the same concentration: Zn^{2+}, Hg^{2+}, Ni^{2+} and Cr^{3+}?

15. Why alternating current is not used for electrolysis?

16. Why do the following statements lack any sense: electrolysis of molten ferric sulphate, electrolysis of molten magnesium carbonate, electrolysis of molten mercuric nitrate, electrolysis of alcohol, electrolysis of sugar?

17. Give examples for the electrolysis of salts when (a) oxygen, (b) chlorine, (c) sulphur are evolved/deposited at the anode.

18. Give examples for the electrolysis of salts when (a) hydrogen, (b) an alkali, (c) a metal are evolved/deposited at the cathode.

19. Write the equations for the chemical processes occurring at the cathode and anode during electrolysis of an aqueous solution of nickel(II) chloride, the anode being made of (a) carbon, (b) nickel.

20. Write the equations to represent the electrolyses of an aqueous sodium hydroxide solution and of molten sodium hydroxide. (a) Platinum and (b) copper anodes are used in both cases.

21. Write the equations for the reactions occurring at insoluble electrodes during electrolysis of aqueous solutions of (a) potassium sulphate, (b) sodium sulphide, (c) lead(II) nitrate, and (d) stannous chloride.

22. Write the equations to represent the reactions that take place at a copper anode during electrolysis of aqueous solutions of (a) $CuSO_4$, (b) NaBr, (c) $Hg(NO_3)_2$ and (d) $ZnCl_2$.

23. Will there be any change in the solution concentration in the process of electrolysis of (a) NaCl, (b) $Ba(NO_3)_2$, (c) $FeSO_4$, (d) K_2CO_3 at platinum electrodes? Write the equations for the reactions that occur in these cases.

24. Write the equations for the reactions that take

place as a result of electrolysis of each of HNO_3 and HBr solutions when (a) direct current and (b) alternating current are passed through these solutions.

25. Show the schemes of electrolyses of molten magnesium and sodium chlorides.

26. Write the molecular equations for the reactions that take place at insoluble electrodes during electrolysis of aqueous solutions of (a) $MgCl_2$, (b) Na_3PO_4, (c) $NiSO_4$, and (d) $Pb(NO_3)_2$.

27. For the following molecular equations representing electrolysis of salt solutions write the schemes showing cathodic and anodic processes:

$$4AgNO_3 + 2H_2O \rightarrow 4Ag + O_2 + 4HNO_3$$
$$Na_2SO_4 + 4H_2O \rightarrow 2H_2 + O_2 + 2NaOH + H_2SO_4$$
$$2ZnCl_2 + 2H_2O \rightarrow H_2 + Zn + Zn(OH)_2 + 2Cl_2$$
$$CaBr_2 + 2H_2O \rightarrow H_2 + Br_2 + Ca(OH)_2$$

Also write these equations in the ionic form.

28. For the following ionic equations representing electrolysis of salt solutions write the molecular equations and also equations which show processes occurring at the cathode and at an insoluble anode:

$$CO_3^{2-} + 3HOH \rightarrow 2OH^- + 2H_2 + O_2 + CO_2$$
$$2Fe^{2+} + 4Cl^- + 2HOH \rightarrow Fe + H_2 + 2Cl_2 + Fe(OH)_2$$
$$4HOH \rightarrow 2H_2 + O_2 + 2OH^- + 2H^+$$
$$S^{2-} + 2HOH \rightarrow H_2 + 2OH^- + S$$

29. What processes occur during electrolyses of molten NaOH, $CuCl_2$ and NaCl?

30. What reactions take place at the electrodes and what products are formed in electrolysis of molten KOH and of aqueous KOH solution?

31. State whether the products, which are deposited at the electrodes in electrolysis of aqueous solutions of each pair of salts taken separately will be the same or not: (a) K_2CO_3 and Na_2SO_4, (b) NaCl and $CaCl_2$, (c) $Ba(NO_3)_2$ and $Pb(NO_3)_2$. Give the respective schemes.

32. Electrolysis of aqueous solutions of which of the following substances results in decomposition of water: potassium chloride, sodium nitrate, sulphuric acid, copper chloride, zinc sulphate and potassium hydroxide?

33. Why does electrolysis of aqueous solutions of calcium nitrate and of potassium hydroxide result in the formation of the same products at the electrodes? Write the schemes for the processes which take place at the electrodes.

34. Why does electrolysis of molten sodium chloride and of an aqueous sodium chloride solution lead to different substances? Write the schemes for the processes which occur at the electrodes.

2.7 PROPERTIES OF OXIDES, HYDROXIDES AND SALTS AS REGARDS THE THEORY OF ATOMIC STRUCTURE AND THE THEORY OF ELECTROLYTIC DISSOCIATION

2.7.1 OXIDES

Compounds consisting of oxygen and a second element are called oxides.

A few examples of oxides are K_2O, CaO, Fe_2O_3, CO_2, P_2O_5, SO_3, Cl_2O_7, OsO_4. All chemical elements, except for He, Ne and Ar, form oxides. The chemical bond between oxygen and the second element in oxides may be ionic or covalent. In terms of chemical properties oxides are classified as salt-forming and non-salt-forming. N_2O, NO and SiO_2 are examples of the latter class. The salt-forming oxides are, in turn, subdivided into basic, acid and amphoteric oxides.

Basic oxides. *Those oxides are called basic oxides whose hydrates are bases.* For example, Na_2O, CuO are basic oxides, since their corresponding hydrates, NaOH and $Cu(OH)_2$, are bases. Mono- and bivalent metal oxides belong, generally, to the basic oxides. The chemical bonding in this case is ionic.

Oxides of alkali metals (Li, Na, K, Rb, Cs, Fr) and those of alkaline-earth metals (Ca, Sr, Ba, Ra) react with water to yield bases. For example:

$$K_2O + H_2O = 2KOH$$

$$BaO + H_2O = Ba(OH)_2$$

The remaining basic oxides do not practically react with water. All basic oxides react with acids to afford salts

and water:

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O$$
$$Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O$$

Basic oxides also react with acid oxides to give salts:

$$FeO + SiO_2 = FeSiO_3$$

Acid oxides. *Oxides whose hydrates are acids are termed as acid oxides.* Nonmetal and metal oxides belong to this class of oxides. For example, N_2O_3, P_2O_5, CrO_3 Mn_2O_7, CO_2, V_2O_5, SO_3, Cl_2O_7 all are acid oxides, because their corresponding hydrates are acids: HNO_2, H_3PO_4, H_2CrO_4, $HMnO_4$, H_2CO_3, H_3VO_4, H_2SO_4, $HClO_4$. The chemical bonding in the acid oxides may be both ionic and covalent. Most acid oxides react with water to yield acids:

$$SO_3 + H_2O = H_2SO_4$$
$$Mn_2O_7 + H_2O = 2HMnO_4$$
$$SiO_2 + H_2O \neq (SiO_2 \text{ does not react with water})$$

Acid oxides react with bases (alkalies) to afford salts and water:

$$N_2O_5 + Ca(OH)_2 = Ca(NO_3)_2 + H_2O$$
$$N_2O_5 + 2OH^- = 2NO_3^- + H_2O$$

Amphoteric oxides. *The metal oxides which, depending upon the medium, exhibit either basic or acidic properties, that is, react with both acids and bases, are called amphoteric oxides.*

Hydrates of amphoteric oxides can exist both in acidic and basic forms. For example,

$$Zn(OH)_2 \leftarrow ZnO \rightarrow H_2ZnO_2$$
$$Al(OH)_3 \leftarrow Al_2O_3 \rightarrow HAlO_2$$

Amphoteric oxides react both with acids and bases:

$$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O$$
$$Al_2O_3 + 6H^+ = 2Al^{3+} + 3H_2O$$
$$Al_2O_3 + 2NaOH + 3H_2O = 2Na[Al(OH)_4]$$
$$Al_2O_3 + 2OH^- + 3H_2O = 2[Al(OH)_4]^-$$

When fused with alkalies, Al_2O_3 affords meta-aluminates:

$$Al_2O_3 + 2NaOH \xrightarrow{\text{fusion}} \underset{\substack{\text{sodium}\\ \text{meta-}\\ \text{aluminate}}}{2NaAlO_2} + H_2O$$

$$Al_2O_3 + 2OH^- = 2AlO_2^- + H_2O$$

The amphoteric oxides do not directly add to water.

2.7.2 HYDROXIDES

Chemical compounds with a general formula R(OH) are called hydroxides, where R stands for an atom or a group of atoms carrying a positive charge.

Depending upon the type of electrolytic dissociation, hydroxides may be divided into three groups: bases, acids, and amphoteric hydroxides. For instance:

$$Ba(OH)_2 \rightleftarrows Ba^{2+} + 2OH^- \quad \text{Base}$$

$$H_2SO_4 \rightleftarrows 2H^+ + SO_4^{2-} \quad \text{Acid}$$

$$Pb^{2+} + 2OH^- \rightleftarrows \underset{\substack{\text{solution}\\ \downarrow\uparrow\\ \text{Pb(OH)}_2\\ \text{precipi-}\\ \text{tate}}}{Pb(OH)_2} \rightleftarrows 2H^+ + PbO_2^{2-} \quad \begin{matrix}\text{Amphoteric}\\ \text{hydroxide}\end{matrix}$$

Bases are electrolytes which on electrolytic dissociation form negative hydroxide ions.

According to a universally accepted nomenclature, compounds containing a hydroxo group are called hydroxides.

If the metal exhibits variable valence, then in the name of the hydroxide the valence of the metal is shown in brackets by a Roman numeral. For example, CuOH is copper(I) hydroxide, $Cu(OH)_2$ is copper(II) hydroxide.

Hydroxides are subdivided into water-soluble and water-insoluble hydroxides. Water-soluble hydroxides are called alkalies. The latter are formed by alkali and alkaline-earth metals. Alkalies react with salt solutions as follows:

$$Pb(NO_3)_2 + 2NaOH = 2NaNO_3 + Pb(OH)_2\downarrow$$

$$Pb^{2+} + 2OH^- = Pb(OH)_2$$

Alkalies may react with several elements as shown below:

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$$

$$Si + 2OH^- + H_2O = SiO_3^{2-} + 2H_2$$

$$2Al + 2NaOH + 6H_2O = 2Na[Al(OH)_4] + 3H_2$$

sodium tetrahydroxoaluminate

$$2Al + 2OH^- + 6H_2O = 2[Al(OH)_4]^- + 3H_2$$

Both water-soluble and water-insoluble hydroxides may react with acids:

$$2Fe(OH)_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 6H_2O$$

$$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$$

Water-insoluble bases undergo thermal decomposition:

$$2Fe(OH)_3 \xrightarrow{t} Fe_2O_3 + 3H_2O$$

Acids are electrolytes electrolytic dissociation of which yields positive hydrogen ions and no other positive ions.

Acids may be (a) solid such as H_3PO_4, H_3BO_3, H_2SiO_3, HPO_3, and liquid such as H_2SO_4, HNO_3, HCl, and so on; (b) strong, e.g., H_2SO_4, HNO_3, HCl, and weak, e.g., H_2SiO_3, H_2SO_3, H_2CO_3, CH_3COOH, H_2S; (c) volatile such as H_2CO_3, H_2SO_3, HNO_3 and hydracids, and nonvolatile, for example, H_2SO_4, H_3PO_4.

Acids react with metals. The reactions between acids and metals are controlled by the acid concentration and activity of the metal. The following five cases are distinguished.

(a) Dilute acids (except for HNO_3) react with those metals which are arranged in the series of standard reduction electrode potentials above hydrogen. One of the products is hydrogen. For example:

$$Fe + H_2SO_4 \text{ (dil.)} = FeSO_4 + H_2\uparrow$$

$$Fe + 2H^+ = Fe^{2+} + H_2$$

(b) Concentrated H_2SO_4 reacts, on heating, with all metals (except for Pt and Au). Hydrogen gas is not evolved in this case. However, sulphur dioxide (SO_2) is formed when heavy metals containing more than five electrons in the *d* orbital are used and hydrogen sulphide (H_2S) gas

is liberated on making use of more active (light, containing less than five *d* electrons) metals:

$$Cu\ (inactive) + 2H_2SO_4\ (conc.) = CuSO_4 + SO_2\uparrow + 2H_2O$$
$$Cu + 4H^+ + SO_4^{2-} = Cu^{2+} + SO_2 + 2H_2O$$
$$8Na\ (active) + 5H_2SO_4\ (conc.) = 4Na_2SO_4 + H_2S\uparrow + 4H_2O$$
$$8Na + 10H^+ + SO_4^{2-} = 8Na^+ + H_2S + 4H_2O$$

(c) Concentrated HNO_3 forms nitrous oxide (N_2O) gas by reacting with alkali and alkaline-earth metals, nitrogen dioxide (NO_2) gas by reacting with other heavy metals. Cold HNO_3 does not react with Fe, Al, Cr, Pt and Au:

$$4Ca + 10HNO_3\ (conc.) = 4Ca(NO_3)_2 + N_2O + 5H_2O$$
$$4Ca + 10H^+ + 2NO_3^- = 4Ca^{2+} + N_2O + 5H_2O$$
$$Cu + 4HNO_3\ (conc.) = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$
$$Cu + 4H^+ + 2NO_3^- = Cu^{2+} + 2NO_2 + 2H_2O$$

(d) Dilute HNO_3 reacts with active metals as well as with Zn, Fe, Sn to evolve ammonia (NH_3) gas or to yield ammonium nitrate ($NH_3 + HNO_3 = NH_4NO_3$). With heavy metals, which have more than five *d* electrons it forms nitric oxide (NO) gas:

$$4Ca + 10HNO_3\ (dil.) = 4Ca(NO_3)_2 + NH_4NO_3 + 3H_2O$$
$$4Ca + 10H^+ + NO_3^- = 4Ca^{2+} + NH_4^+ + 3H_2O$$
$$3Cu + 8HNO_3\ (dil.) = 3Cu(NO_3)_2 + 2NO + 4H_2O$$
$$3Cu + 8H^+ + 2NO_3^- = 3Cu^{2+} + 2NO + 4H_2O$$

(e) Weak acids like H_2CO_3, H_2SO_3, CH_3COOH react only with active metals:

$$2CH_3COOH + Mg = Mg(CH_3COO)_2 + H_2$$
$$2H^+ + Mg = Mg^{2+} + H_2$$

All acids react with basic and amphoteric oxides to afford salts and water.

While considering reactions of acids with salts, it is necessary that the state of aggregation of the salts be taken into account. Acids react with salt solutions only in that case when a precipitate is formed or a gas is evolved:

$$H_2SO_4 + Ba(NO_3)_2\ (solution) = BaSO_4\downarrow + 2HNO_3$$
$$SO_4^{2-} + Ba^{2+} = BaSO_4$$

When the salts are in a solid state of aggregation, salts of weak acids are employed for reaction:

$$2HCl + K_2CO_3(s) = 2KCl + H_2O + CO_2\uparrow$$
$$2H^+ + CO_3^{2-} = H_2O + CO_2$$

Amphoteric hydroxides in aqueous solutions react as both acid and base, that is, exhibit amphoteric properties. Aqueous solutions of such substances contain simultaneously two opposite carriers which have acidic properties (hydrogen ions) and basic properties (hydroxide ions):

$$\begin{array}{ccccc} & & Zn(OH)_2 & & \\ & & \text{precipitate} & & \\ & & \downarrow\uparrow & & \\ 2H^+ + ZnO_2^{2-} & \rightleftharpoons & Zn(OH)_2 & \rightleftharpoons & Zn^{2+} + 2OH^- \\ \text{An acid-type dissociation (in an alkaline medium)} & & \text{solution} & & \text{A base-type dissociation (in an acidic medium)} \end{array}$$

2.7.3 SALTS

Depending upon the composition, salts are divided into three types: neutral, acid and basic.

Neutral or normal salts may be considered as the products of complete substitution of hydrogen atoms in acids for metal atoms or as the products of complete substitution of hydroxyl groups in bases for acid residues. The complete substitution of hydrogen atoms, for example, in H_3PO_4 for metals may result in Na_3PO_4, $Ca_3(PO_4)_2$, $AlPO_4$. On the other hand, replacement of hydroxyl groups in $Al(OH)_3$ by acid residues may produce salts like $AlCl_3$, $Al_2(SO_4)_3$, $AlPO_4$.

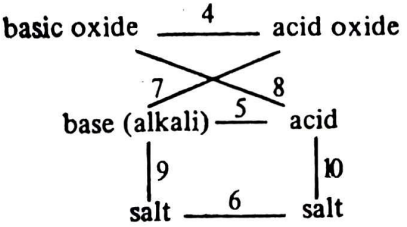
Acid salts are the products of incomplete substitution of hydrogen atoms in polybasic acids for metals. Dibasic acids give only one type of acid salt. For example, sulphurous acid, H_2SO_3, can produce potassium hydrogen sulphite, $KHSO_3$, calcium hydrogen sulphite, $Ca(HSO_3)_2$, and so on.

Tribasic acids yield two types of acid salts. Phosphoric acid, H_3PO_4, for instance, affords calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$, and calcium hydrogen phosphate, $CaHPO_4$.

Basic salts are the products of incomplete substitution of hydroxo groups in polyacid bases for acid residues. For example, by replacing successively one and two hydroxo groups in $Al(OH)_3$ one gets basic salts, dihydroxoaluminium chloride, $Al(OH)_2Cl$, and hydroxoaluminium chloride, $AlOHCl_2$, respectively.

Preparation of salts. There are several methods for the preparation of neutral salts. Here we are going to deal with only main ten of them:

1. metal + nonmetal
2. metal + acid
3. metal + salt



The above schemes, according to which neutral salts can be formed, are being illustrated below by examples.

1. Reaction of a metal with a nonmetal:

$$2Na + Cl_2 = 2NaCl$$

2. Reaction of acids with metals. All dilute acids (except for nitric acid) react with metals arranged in the series of standard reduction electrode potentials above hydrogen:

$$Fe + 2HCl = FeCl_2 + H_2\uparrow$$
$$Fe + 2H^+ = Fe^{2+} + H_2$$

3. Reaction of a metal with salts. A more active metal replaces a less active metal from the salt solution of the latter:

$$Fe + CuSO_4 = Cu + FeSO_4$$
$$Fe + Cu^{2+} = Cu + Fe^{2+}$$

4. Reaction between basic and acid oxides:

$$CaO + CO_2 = CaCO_3$$

5. Reaction between an acid and a hydroxide:

$$H_2SO_4 + Zn(OH)_2 = ZnSO_4 + 2H_2O$$
$$2H^+ + Zn(OH)_2 = Zn^{2+} + 2H_2O$$

6. Reaction between two salts. In this case, both the reactant salts should be water-soluble. One of the produced salts should, however, be in precipitate, that is, insoluble after the reaction is over:

$$AgNO_3 + NaCl = AgCl\downarrow + NaNO_3$$
$$Ag^+ + Cl^- = AgCl\downarrow$$

7. Reaction of an alkali with an acid oxide:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$
$$2OH^- + CO_2 = CO_3^{2-} + H_2O$$

8. Reaction between a basic oxide and an acid:

$$CuO + 2HCl = CuCl_2 + H_2O$$
$$CuO + 2H^+ = Cu^{2+} + H_2O$$

9. Reaction of salts with alkalies:

$$CuSO_4 + 2KOH = K_2SO_4 + Cu(OH)_2\downarrow$$
$$Cu^{2+} + 2OH^- = Cu(OH)_2\downarrow$$

10. Reaction of salts with acids:

$$BaCl_2 + H_2SO_4 = BaSO_4\downarrow + 2HCl$$
$$Ba^{2+} + SO_4^{2-} = BaSO_4\downarrow$$

The reaction between acids and salts has already been discussed in Section 2.7.2. Of the ten reactions discussed above, reactions 3, 6, 9 and 10 describe the chemical properties of neutral salts. However, not all the ten reactions mentioned above can be carried out practically for preparing a specific salt. In each particular case, it is necessary to take into account the reaction conditions and the properties of the reacting substances.

Acid salts can be prepared by reacting (a) a base with an excess acid

$$NaOH + H_2SO_3 = NaHSO_3 + H_2O$$

(b) a neutral salt with an excess acid:

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2$$
$$Ca_3(PO_4)_2 + 2H_2SO_4 = Ca(H_2PO_4)_2 + 2CaSO_4$$

To convert an acid salt into a neutral one, an alkali is to be added:

$$NaHSO_3 + NaOH = Na_2SO_3 + H_2O$$
$$Ca(H_2PO_4)_2 + 2Ca(OH)_2 = Ca_3(PO_4)_2 + 4H_2O$$

Basic salts may be prepared (a) by the action of an excess base on an acid:

$$Ca(OH)_2 + HCl = CaOHCl + H_2O$$

(b) by reacting an alkali with an excess neutral salt:

$$2CoSO_4 + 2NaOH = (CoOH)_2SO_4 + Na_2SO_4$$

To convert a basic salt into a neutral one, an acid is to be added:

$$(CoOH)_2SO_4 + H_2SO_4 = 2CoSO_4 + 2H_2O$$

It should be pointed out that basic salts are less soluble than the neutral ones. Like the neutral salts, they react with acids and salts. The acid salts, on the other hand, are more soluble than the neutral ones. For example, $Ca_3(PO_4)_2$ is insoluble in water, $CaHPO_4$ is sparingly soluble, while $Ca(H_2PO_4)_2$ is fairly soluble.

PROBLEMS AND EXERCISES

1. Which compounds are termed as oxides?

2. Which oxides are called basic, acid and amphoteric oxides?

3. Cite examples of acid, basic, amphoteric and indifferent oxides.

4. Name the following oxides: N_2O, SO_2, Mn_2O_7, CO, Cr_2O_3, P_2O_5, B_2O_3, SnO_2, CuO, OsO_4 and SeO_3.

5. What naturally occurring oxides do you know?

6. Why such oxides as calcium oxide and phosphorus pentoxide do not occur in nature?

7. Give examples of hydrating oxides.

8. Give examples of nonhydrating oxides.

9. Which compounds are known as hydroxides?

10. Name the following compounds: $Mg(OH)_2$, KOH, $Cr(OH)_3$, $CuOH$, $Cu(OH)_2$, $LiOH$, $Fe(OH)_3$ and $Fe(OH)_2$.

11. Name the following acids: HNO_2, H_2SO_4, H_3PO_4, HCl, HNO_3, H_2SO_3, H_3BO_3, HI, CH_3COOH, H_2S, H_2SiO_3 and HBr.

12. Which substances are called salts?

13. List the types of salts known to you.

14. Name the following salts: $Al_2(SO_4)_3$, $FeOH(NO_3)$, KHS, $FeCl_2$, NaH_2PO_4, $AlOHSO_4$, $Ca(NO_3)_2$, $Ca(HCO_3)_2$,

$BiOH(NO_3)_2$, $Ba_3(PO_4)_2$, $KHSO_3$, $Cu_2(OH)_2CO_3$, K_2SiO_3, $Pb(HSO_3)_2$ and $MgOHCl$.

15. Name the following iron salts and write the graphic formulas for them: $Fe(OH)_2NO_3$, $FeOHCl$, $FeClNO_3$, $FeNO_3SO_4$, $FeOHNO_2$, $FeHPO_4$, $Fe_2(SO_4)_3$, $(FeOH)_2SO_4$, $FeOHSO_4$, $FeK(SO_4)_2$.

16. Write the equations for the reactions between (a) silicon dioxide and ferrous oxide, (b) cupric oxide and sulphur dioxide, (c) dinitrogen pentoxide and calcium oxide, (d) phosphorus pentoxide and sodium oxide, (e) magnesium oxide and sulphur dioxide and (f) dinitrogen trioxide and barium oxide. Name the type of chemical bond involved in each of the above oxides.

17. Which of the following compounds may react with dinitrogen pentoxide: $Ca(OH)_2$, H_2SO_4, $MgCl_2$, H_2O, SO_2, K_2O? Write the ionic equations to represent the possible reactions.

18. Complete the equations for the following reactions:

$$KOH + SO_3 \rightarrow \ldots \qquad Ca(OH)_2 + CO_2 \rightarrow \ldots$$
$$F_2O_3 + H_2SO_4 \rightarrow \ldots \qquad Al_2O_3 + HNO_3 \rightarrow \ldots$$
$$LiOH + Cl_2O_7 \rightarrow \ldots \qquad CaO + H_3PO_4 \rightarrow \ldots$$

Write each of these equations both in molecular and ionic forms.

19. Which of the following compounds will react with potassium hydroxide: $Mg(OH)_2$, Cl_2O_7, H_2SO_3, $CuCl_2$, Al_2O_3, BaO and $Zn(OH)_2$? Write the equations for the possible reactions in molecular and ionic forms.

20. Write the equations in molecular and ionic forms for the reactions between the relevant acids and hydroxides to yield the following salts: $FeOHSO_4$, $NaHCO_3$, $Mg(NO_3)_2$, $Ca_3(PO_4)_2$ and $Al_2(SO_4)_3$.

21. Complete the equations for the following reactions, yielding salts, both in molecular and ionic forms:

$$ZnO + KOH \rightarrow \ldots \qquad Al_2O_3 + NaOH \rightarrow \ldots$$
$$Sn(OH)_2 + NaOH \rightarrow \ldots \qquad Zn + KOH \rightarrow \ldots$$

22. Of the following compounds which will react with hydrochloric acid: H_2SO_4, CuO, P_2O_5, $AgNO_3$, $Fe(OH)_3$, $MgSO_4$ and K_2CO_3? Write the equations for the possible reactions in molecular and ionic forms.

23. Complete the equations for the reactions, which are used for the preparation of salts, both in molecular

and ionic forms:

$Ca + H_3PO_4 \rightarrow \ldots$ $\quad Fe + HCl \rightarrow \ldots$

$Fe_2O_3 + H_2SO_4 \rightarrow \ldots$ $\quad Ba(OH)_2 + H_3AsO_4 \rightarrow \ldots$

$Mg + H_2SO_4 \rightarrow \ldots$ $\quad K_2O + H_2SO_3 \rightarrow \ldots$

$Al(OH)_3 + HClO_4 \rightarrow \ldots$ $\quad LiOH + H_2CrO_4 \rightarrow \ldots$

$CaO + HNO_3 \rightarrow \ldots$ $\quad Fe(OH)_2 + H_2SeO_4 \rightarrow \ldots$

24. Write the equations for the reactions, yielding neutral salts, between (a) sodium silicate and nitric acid, (b) calcium bicarbonate and hydrobromic acid, (c) potassium bisulphate and potassium hydroxide, (d) aluminium hydroxosulphate and sulphuric acid, (e) aluminium hydroxoacetate and acetic acid, (f) calcium bisulphide and calcium hydroxide.

25. Write the equations in molecular and ionic forms for the reactions which occur when the following transformations are carried out:

$CaO \rightarrow Ca(OH)_2$, $CaO \rightarrow CaCl_2$

$SO_3 \rightarrow H_2SO_4$, $SO_3 \rightarrow CaSO_4$

$K_2O \rightarrow KOH$, $K_2O \rightarrow K_2SO_4$

$P_2O_5 \rightarrow H_3PO_4$, $P_2O_5 \rightarrow K_3PO_4$

$Fe_2O_3 \rightarrow Fe_2(SO_4)_3$, $Fe_2O_3 \rightarrow FeCl_3$

$CO_2 \rightarrow NaHCO_3$, $CO_2 \rightarrow Na_2CO_3$

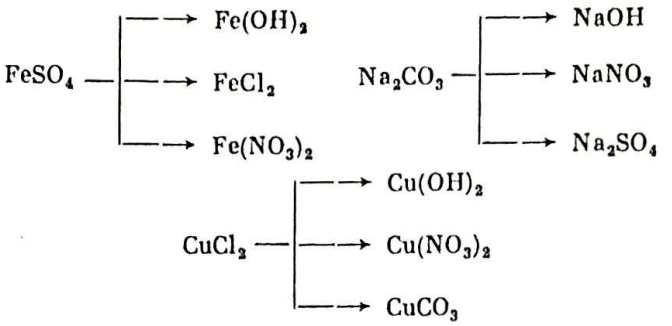
26. Write the equations in molecular and ionic forms for the reactions to bring about the following transformations:

$Ca(OH)_2 \rightarrow Ca(NO_3)_2$, $Ca(OH)_2 \rightarrow CaCO_3$

$H_2SO_4 \rightarrow H_2S$, $H_2SO_4 \rightarrow SO_2$

$MgCl_2 \rightarrow Mg(NO_3)_2$, $MgCl_2 \rightarrow MgCO_3$

27. Write the equations in molecular and ionic forms for the reactions with the help of which the following transformations may be carried out:



28. Complete the equations for the following reactions and write their molecular and ionic forms:

$Al_2(SO_4)_3+Ba(NO_3)_2 \rightarrow \ldots$
$FeCl_3+KOH \rightarrow \ldots$
$Na_2CO_3+Ca(OH)_2 \rightarrow \ldots$
$Na_2SiO_3+HCl \rightarrow \ldots$

29. Complete the equations and give their ionic forms:

$CuSO_4+NaOH \rightarrow \ldots$ $CuO+HNO_3 \rightarrow \ldots$
$CuCl_2+K_2CO_3 \rightarrow \ldots$ $Cu(OH)_2+HCl \rightarrow \ldots$

30. Complete the equations of the reactions yielding basic salts and write their molecular and ionic forms:

$Al(OH)_3+HNO_3 \rightarrow \ldots$ $Cu(OH)_2+HNO_3 \rightarrow \ldots$
$Mg(OH)_2+HCl \rightarrow \ldots$ $Zn(OH)_2+H_3AsO_4 \rightarrow \ldots$
$Fe_2(SO_4)_3+NaOH \rightarrow \ldots$ $Fe(OH)_3+H_2SO_4 \rightarrow \ldots$

31. Complete the equations of the reaction leading to acid salts, both in molecular and ionic forms:

$NaOH+H_2CO_3 \rightarrow \ldots$ $NaOH+H_2S \rightarrow \ldots$
$Ba(OH)_2+H_3PO_4 \rightarrow \ldots$ $KOH+H_2SO_4 \rightarrow \ldots$
$KOH+H_3PO_4 \rightarrow \ldots$ $Ca(OH)_2+H_2CO_3 \rightarrow \ldots$

32. Write the equations in molecular and ionic forms for the reactions between (a) ferric chloride and sodium phosphate, (b) cupric sulphate and sodium phosphate, (c) hydrogen sulphide and cupric nitrate, (d) potassium

sulphite and zinc sulphate, (e) sodium sulphite and magnesium nitrate, (f) potassium carbonate and barium sulphide, and (g) sodium silicate and calcium bromide.

33. Write the equations in molecular and ionic forms for the reactions between (a) magnesium hydroxochloride and sodium hydroxide, (b) ferric hydroxosulphate and sulphuric acid, (c) calcium biphosphate and calcium hydroxide, (d) potassium bisulphide and potassium hydroxide, and (e) barium dihydrogen phosphate and barium hydroxide.

34. Write the equations in molecular and ionic forms for the reactions involved in the following transformations: (a) $CuO \rightarrow CuCl_2 \rightarrow Cu(NO_3)_2$, (b) $CaO \rightarrow$ $\rightarrow Ca(OH)_2 \rightarrow Ca(NO_3)_2$, (c) $MgO \rightarrow MgSO_4 \rightarrow MgCl_2$

35. Write the equations in molecular and ionic forms for the reactions with the help of which the following transformations may be carried out:

$$SO_2 \rightarrow H_2SO_3 \rightarrow KHSO_3 \rightarrow K_2SO_3$$
$$P_2O_5 \rightarrow H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \rightarrow Ca_3(PO_4)_2$$
$$CO_2 \rightarrow Ca(HCO_3)_2 \rightarrow CaCO_3 \rightarrow CaCl_2$$

36. Write the molecular and ionic forms for the reactions needed to bring about the following transformations:

$$PbO \rightarrow Pb(NO_3)_2 \rightarrow Na_2PbO_2 \rightarrow Pb(OH)_2$$
$$ZnO \rightarrow ZnSO_4 \rightarrow Na_2ZnO_2 \rightarrow Zn(OH)_2$$
$$Al_2O_3 \rightarrow AlCl_3 \rightarrow NaAlO_2 \rightarrow Al(OH)_3$$

37. Write the equations in molecular and ionic forms for the reactions with the help of which the following transformations may be carried out:

$$ZnSO_4 \rightarrow Zn(OH)_2 \rightarrow ZnCl_2 \rightarrow Zn$$
$$AlCl_3 \rightarrow Al(NO_3)_3 \rightarrow Al(OH)_3 \rightarrow NaAlO_2$$
$$Pb(NO_3)_2 \rightarrow Pb(OH)_2 \rightarrow PbO \rightarrow Na_2PbO_2$$

38. Write the molecular and ionic forms for the reactions which can bring about the following transformations:

$$Fe_2(SO_4)_3 \rightarrow FeCl_3 \rightarrow Fe(OH)_3 \rightarrow FeOH(NO_3)_2$$
$$K \rightarrow KOH \rightarrow KHSO_4 \rightarrow K_2SO_4 \rightarrow KCl \rightarrow KNO_3$$
$$Cu(OH)_2 \rightarrow CuOHNO_3 \rightarrow Cu(NO_3)_2 \rightarrow CuSO_4$$

39. Write the molecular and ionic forms for the reactions with the aid of which the following transforma-

tions may be carried out:

$$Ca \rightarrow Ca(OH)_2 \rightarrow CaCl_2 \rightarrow Ca(NO_3)_2 \rightarrow CaSO_4$$
$$Cu \rightarrow Cu(NO_3)_2 \rightarrow Cu(OH_2) \rightarrow CuSO_4 \rightarrow Al_2(SO_4)_3$$
$$Mg \rightarrow MgSO_4 \rightarrow MgCl_2 \rightarrow MgOHCl \rightarrow Mg(OH)_2$$

40. Write the molecular and ionic forms for the reactions involved in the following transformations:

$$CuSO_4 \rightarrow CuCl_2 \rightarrow ZnCl_2 \rightarrow Na_2ZnO_2 \rightarrow Zn(OH)_2$$
$$Hg(NO_3)_2 \rightarrow Al(NO_3)_3 \rightarrow NaAlO_2 \rightarrow Al(OH)_3 \rightarrow AlOHCl_2$$
$$ZnSO_4 \rightarrow Zn(OH_2) \rightarrow ZnCl_2 \rightarrow AlCl_3 \rightarrow Al(OH)_3$$

41. Write the equations both in molecular and ionic forms for the reactions that occur when the following conversions are brought about:

$$CuCl_2 \rightarrow Cu(OH)_2 \rightarrow CuSO_4 \rightarrow ZnSO_4 \rightarrow Na_2ZnO_2$$
$$Fe(NO_3)_3 \rightarrow FeOH(NO_3)_2 \rightarrow Fe(OH)_3 \rightarrow FeCl_3 \rightarrow Fe(NO_3)_3$$
$$Al_2O_3 \rightarrow AlCl_3 \rightarrow Al(OH)_3 \rightarrow NaAlO_2 \rightarrow NaNO_3$$
$$Mg(OH)_2 \rightarrow MgSO_4 \rightarrow MgCl_2 \rightarrow Mg(NO_3)_2 \rightarrow Mg(OH)_2$$

42. Calculate the mass of calcium oxide required to prepare 3.7 g of calcium hydroxide.

43. Carbon monoxide may be prepared by reacting carbon with ferric oxide. Write the equation for this reaction. Also calculate how many litres of carbon monoxide may be obtained from 80 g of ferric oxide.

44. How many grams of sulphur trioxide are required to prepare 270 grams of potassium sulphate?

45. Calculate the amount of aluminium oxide required to obtain 213 grams of $Al(NO_3)_3$.

46. How many moles of carbon dioxide are needed to form 0.5 mole of $Ca(HCO_3)_2$?

47. Determine the formulas of the acids having the following compositions: (a) 2.1% H, 29.8% N, and 68.1% O and (b) 3.7% H, 37.8% P, and 58.5% O.

48. How many grams of sodium hydroxide having 10% by mass of NaOH will be required to neutralize 20 g of sulphuric acid containing 4.9% by mass of H_2SO_4?

49. By reacting 0.1 mole of sodium oxide with water how much sodium hydroxide will be obtained?

50. How many grams of hydrogen will be liberated when 11.2 g of iron are treated with hydrochloric acid?

51. How many litres of hydrogen gas measured at STP may be obtained when 24 g of zinc are treated with excess dilute sulphuric acid?

52. A mass of 2.5 g of a mixture of cupric oxide and metallic copper was treated with 3.6 g of a hydrochloric acid solution which was taken in excess. How much acid was required to dissolve the mixture? What is the composition of the mixture?

53. A volume of 0.56 litre of hydrogen measured at STP was liberated when 1.4 g of a bivalent metal were treated with an acid. Name this metal.

54. An excess of barium chloride was reacted with sulphuric acid, as a result of which a mass of 699 g of barium sulphate precipitated. Calculate the amount of sulphuric acid consumed.

55. By treating 1 kg of phosphorite, containing 62% by mass of $Ca_3(PO_4)_2$, with sulphuric acid a mass of 0.910 kg of superphosphate, $Ca_3(PO_4)_2 + 2CaSO_4$, was isolated. What mass percent of the theoretical amount of superphosphate was yielded?

56. How many grams of concentrated nitric acid are required to oxidize 8 g of copper to copper nitrate?

57. To prepare a mass of 26.4 g of ammonium sulphate, what amounts of ammonia and sulphuric acid will be required?

58. To form a mass of 132 g of carbon dioxide, how many grams of hydrochloric acid should react with calcium carbonate?

59. How many grams of potassium hydroxide should be taken to neutralize 0.5 mole of sulphuric acid?

60. To a solution containing 5.4 g of cupric chloride a solution containing 1.7 g of hydrogen sulphide was added. The whole solution was then concentrated to a small volume. Determine the amount and mass of the precipitate thus formed.

61. A mass of 9.09 g of a precipitate was formed by reacting an excess potassium sulphate with a solution of lead(II) nitrate. How many grams of lead(II) nitrate were there in the solution?

62. 0.24 mole of sodium hydroxide was added to a solution containing 0.2 mole of ferric chloride. How many moles of iron hydroxide were formed as a result of this

reaction and how many grams of ferric chloride remained unreacted in the solution?

63. How many litres of carbon dioxide measured at STP are formed when a mass of 8 g of a compound containing 75% by mass of C and 25% by mass of H is burnt?

64. How many grams of potassium hydroxide are required to convert 70 g of sulphuric acid to the respective acid salt?

3
GROUP VA ELEMENTS

Group VA of the periodic table contains nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), and bismuth (Bi). This Group is also referred to as the nitrogen family.

The first two elements, nitrogen and phosphorus, are typical nonmetals, arsenic and antimony occupy an intermediate position, while bismuth is a metal. Nitrogen can form stable diatomic molecules, N_2. Phosphorus, arsenic and antimony are known to have tetrahedral structures (P_4, As_4, Sb_4), while ordinary forms for arsenic and antimony (As and Sb) are also known. Bismuth can exist only in the metallic state, Bi.

Each of these elements has five electrons in the outermost layer (or shell). So they are short of three electrons to attain an octaelectronic configuration. All these elements are capable of completing their outermost shell. For example, in compounds with hydrogen these elements are strictly trivalent. The electronegativities of the elements of the nitrogen family, however, decrease with increasing their atomic number.

On the other hand, atoms of these elements may give up electrons. In oxycompounds and in compounds with halogens (except for iodine) and sulphur, these elements exhibit valences of three and five.

All hydroxides formed by the Group VA elements in pentavalent state are acidic in nature. The strength of these acids decreases down the Group. For example, HNO_3 is a strong acid, H_3PO_4 is a moderately weak acid,

H_3AsO_4 is a weak acid, while the remaining two acids are very weak.

Nitrogen and phosphorus exist in all their compounds as anions, whereas arsenic, antimony and bismuth have a tendency to form cations. For instance, these three elements are present in aqueous solutions as cations with oxidation number of $+3$ ($\overset{+3}{As}$, $\overset{+3}{Sb}$, $\overset{+3}{Bi}$), in a very insignificant amount, since their salts undergo hydrolysis.

Table 3.1 Simplest Compounds Formed by Group VA Elements

Element	Valence	Oxides	Compounds with hydrogen	Acid
Nitrogen	III, V	N_2O, NO_2, NO, N_2O_3, N_2O_5	NH_3 (ammonia)	HNO_3 (nitric)
Phosphorus	III, V	P_2O_3, P_2O_5	PH_3 (phosphine)	H_3PO_4 (phosphoric)
Arsenic	III, V	As_2O_3, As_2O_5	AsH_3 (arsine)	H_3AsO_4 (arsenic)
Antimony	III, V	Sb_2O_3, Sb_2O_5	SbH_3 (stibine)	$H[Sb(OH)_6]$ (antimonic)
Bismuth	III, V	Bi_2O_3, Bi_2O_5	BiH_3 (bismuth hydride)	$Bi_2O_5 \cdot H_2O$ or $HBiO_3$ * (bismuthic)

* For bismuth the formula of the acid has not been established, while the salts of this acid have definite compositions.

In this way, though the elements under question are arranged in the same subgroup, they differ from one another in many properties. Let us discuss the properties of nitrogen, phosphorus and their compounds.

3.1 NITROGEN AND ITS COMPOUNDS

In free state nitrogen is chemically inert. It does not occur in nature in the form of inorganic compounds. Nitrogen reacts with simple substances (except for Li) either at elevated temperature, or in the presence of catalysts. In compounds its oxidation number varies from -3 to $+5$. Nitrogen forms five oxides with oxygen. These are acidic oxides (N_2O_3, NO_2, and N_2O_5) and nonsalt-forming

oxides (N_2O and NO). The acids and salts corresponding to the acidic oxides are nitrous acid, HNO_2, and nitrites for N_2O_3 and nitric acid, HNO_3, and nitrates for N_2O_5, respectively. NO_2 forms a mixture of HNO_3 and HNO_2. Nitric acid belongs to strong electrolytes and exhibits strong oxidizing properties. Salts of nitric acid decompose on heating to yield oxygen.

Example 1. How can the following transformations be realized: $(NH_4)_3PO_4 \rightarrow NH_3 \rightarrow NH_4NO_2 \rightarrow N_2 \rightarrow$ $\rightarrow NO \rightarrow NO_2 \rightarrow HNO_3 \rightarrow Hg(NO_3)_2 \rightarrow NO_2$? Write the equations for each step in molecular and ionic forms. For redox reactions write the electronic equations. Also indicate the reaction conditions for each step.

Solution. 1. Ammonium salts formed by non-volatile acids yield ammonia on heating:

$$(NH_4)_3PO_4 \xrightleftharpoons{t} 3NH_3\uparrow + H_3PO_4$$

2. Ammonia reacts vigorously with acid:

$$NH_3 + HNO_2 = NH_4NO_2$$
$$NH_3 + HNO_2 = NH_4^+ + NO_2^-$$

3. On decomposition, ammonium nitrite affords nitrogen:

$$\overset{-3}{N}H_4\overset{+3}{N}O_2 \xrightleftharpoons{t} \overset{0}{N}_2 + 2H_2O$$

$$\begin{array}{l|l} \overset{-3}{N} - 3e^- \rightarrow \overset{0}{N} & \times 1 \\ \overset{+3}{N} + 3e^- \rightarrow \overset{0}{N} & \times 1 \end{array}$$

4. At elevated temperatures (using electrical arc, discharge due to lightning) nitrogen combines with oxygen as follows:

$$N_2 + O_2 = 2NO$$

5. Under ordinary conditions NO enters into reaction with oxygen of air to yield NO_2:

$$2\overset{+2}{N}O + O_2 = 2\overset{+4}{N}O_2$$

$$\begin{array}{l|l} \overset{+2}{N} - 2e^- = \overset{+4}{N} & \times 2 \\ O_2 + 4e^- = 2\overset{-2}{O} & \times 1 \end{array}$$

6. On dissolution in water, NO_2 gives nitric and nitrous acids:

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

Nitrous acid is unstable and, hence, decomposes:

$$3\overset{+3}{H}\overset{+5}{N}O_2 = \overset{+5}{H}\overset{+5}{N}O_3 + 2\overset{+2}{N}O + H_2O$$

$$\begin{array}{l|l} \overset{+3}{N} - 2e^- \rightarrow \overset{+5}{N} & \times 1 \\ \overset{+3}{N} + 1e^- \rightarrow \overset{+2}{N} & \times 2 \end{array}$$

Therefore, the overall reaction between NO_2 and water may be written as

$$3NO_2 + H_2O = 2HNO_3 + NO$$

To prevent the liberation of nitric oxide, the reaction is carried out in the presence of oxygen of air:

$$4\overset{+4}{N}O_2 + 2H_2O + \overset{0}{O}_2 = 4\overset{+5}{H}\overset{+5}{N}O_3$$

$$\begin{array}{l|l} \overset{+4}{N} - e^- \rightarrow \overset{+5}{N} & \times 4 \\ \overset{0}{O}_2 + 4e^- \rightarrow 2\overset{-2}{O} & \times 1 \end{array}$$

7. Nitric acid is an oxidizing agent and reacts with metals arranged in the series of standard reduction electrode potentials below hydrogen. Depending upon the acid concentration, either NO gas (with dilute HNO_3), or NO_2 gas (when concentrated HNO_3 is employed) is formed:

$$3\overset{0}{H}g + 8\overset{+5}{H}\overset{+5}{N}O_3 \text{ (dil.)} = 3\overset{+2}{H}g(NO_3)_2 + 2\overset{+2}{N}O + 4H_2O$$

$$\begin{array}{l|l} \overset{0}{Hg} - 2e^- \rightarrow \overset{+2}{Hg} & \times 3 \\ \overset{+5}{N} + 3e^- \rightarrow \overset{+2}{N} & \times 2 \end{array}$$

$$3Hg + 8H^+ + 2NO_3^- = 3Hg^{2+} + 2NO + 4H_2O$$

The reaction may also be carried out with mercuric oxide:

$$HgO + 2HNO_3 = Hg(NO_3)_2 + H_2O$$

$$HgO + 2H^+ = Hg^{2+} + H_2O$$

8. Nitrates of heavy metals lying in the series of standard reduction electrode potentials after copper decompose to free metal, nitrogen dioxide and oxygen:

$$2Hg(NO_3)_2 = 2Hg + 4NO_2 + O_2$$

$$\begin{array}{l|l} \left.\begin{array}{l} \overset{+5}{2N} + 2e^- \rightarrow \overset{+4}{2N} \\ \overset{+2}{Hg} + 2e^- \rightarrow \overset{0}{Hg} \end{array}\right\} & \times 1 \\ \overset{-2}{2O} - 4e^- \rightarrow \overset{0}{O}_2 & \times 1 \end{array}$$

Example 2. 89.6 litres of a mixture of nitrogen and hydrogen measured at STP were passed over a catalyst. After the reaction, the volume of the mixture reduced to 67.2 litres. Ammonia thus formed was dissolved in 101 ml of an aqueous ammonia solution of density 0.95 g/ml containing 12% by mass of NH_4OH. Determine the percent strength of the final solution.

Solution. 1. First let us determine the decrease in volume of the mixture: 89.6 — 67.2 = 22.4 litres.

2. It is seen from the reaction equation $N_2 + 3H_2 \rightleftarrows 2NH_3$ that the two gases (N_2 and H_2) react in a 1:3 ratio and the volume of the obtained ammonia is twice as low as that of the starting gases. The change in the volume of the mixture equals the volume of gaseous ammonia formed. It means that in the given case 22.4 litres of ammonia have been formed for which 11.2 litres of nitrogen and 33.6 litres of hydrogen have been consumed.

3. A volume of 22.4 litres of ammonia measured at STP has a mass of 17 g. Therefore, the mass of the solution has increased by 17 g.

4. The mass of the solution with a density of 0.95 g/ml is: 101 ml × 0.95 g/ml = 95.95 g.

5. The mass of ammonia in a solution containing 12% by mass of NH_4OH is equal to

$$m = m_1 w = 95.95 \text{ g} \times 0.12 = 11.514 \text{ g}$$

6. 17 g of ammonia react with water by the following equation

$$NH_3 + H_2O = NH_4OH\downarrow$$

and form 35 g of NH_4OH.

7. So the mass of NH_4OH in the final solution is

$$11.514 + 35 = 46.514 \text{ g}$$

8. On the other hand, the mass of the final solution is

$$95.95 + 17 = 112.95 \text{ g}$$

9. Therefore, the percent strength of the final solution is:

$$w = (m/m_1) \times 100\% = (46.514 \text{ g}/112.95 \text{ g}) \times 100\% = 41.2\%$$

Example 3. A mixture of gases liberated upon decomposition of 33.1 g of lead(II) nitrate is dissolved in 10 ml of water. Which acid is formed as a result and what is its percent strength? What is the mass of 0.1 *M* potassium hydroxide solution with a density of 1.05 g/ml required to neutralize this acid?

Solution. 1. The mass of nitrogen dioxide evolved upon decomposition of 33.1 g of $Pb(NO_3)_2$ may be calculated on the basis of the equation $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$ as follows:

$$2 \times 331 \text{ g of } Pb(NO_3)_2 \text{ yield } 4 \times 46 \text{ g of } NO_2$$

$$33.1 \text{ g of } Pb(NO_3)_2 \text{ yield } 33.1 \text{ g} \times 4 \times 46 \text{ g}/(2 \times 331 \text{ g}) = 9.2 \text{ g of } NO_2$$

2. Likewise, the mass of oxygen liberated when 33.1 g of $Pb(NO_3)_2$ are decomposed may be calculated:

$$2 \times 331 \text{ g of } Pb(NO_3)_2 \text{ afford } 32 \text{ g of } O_2$$

$$33.1 \text{ g of } Pb(NO_3)_2 \text{ afford } 33.1 \text{ g} \times 32 \text{ g}/(2 \times 331 \text{ g}) = 1.6 \text{ g of } O_2$$

3. The mass of nitric acid formed from 9.2 g of NO_2 is calculated following the equation

$$4NO_2 + 2H_2O + O_2 = 4HNO_3$$

$$4 \times 46 \text{ g of } NO_2 \text{ lead to } 4 \times 63 \text{ g } HNO_3$$

$$9.2 \text{ g of } NO_2 \text{ lead to } 9.2 \text{ g} \times 4 \times 63 \text{ g}/(4 \times 46 \text{ g}) = 12.6 \text{ g of } HNO_3$$

Now we shall find the mass of nitric acid solution which has resulted from dissolution of 9.2 g of NO_2 and 1.6 g of O_2 in 10 ml of water: 1.6 + 9.2 + 10 = 20.8 g. This mass of solution contains 12.6 g of the acid.

4. Now we shall calculate the percent strength of the nitric acid:

$$20.8 \text{ g of the solution contains } 12.6 \text{ g of } HNO_3$$

$$100 \text{ g of the solution contains } 100 \text{ g} \times 12.6 \text{ g}/20.8 \text{ g} = 60.6 \text{ g of } HNO_3$$

Therefore, the percent strength of the HNO_3 solution is 60.6%.

5. The mass of KOH required to neutralize 12.6 g of HNO_3 is calculated from the equation

$$KOH + HNO_3 = KNO_3 + H_2O$$

63 g of HNO_3 require 56 g of KOH

12.6 g of HNO_3 require $(12.6 \times 56)/63$ g $= 11.2$ g of KOH

6. The volume of 0.1 *M* KOH solution required to neutralize the acid is determined as follows:

5.6 g of KOH are present in 1000 ml of 0.1 *M* KOH solution

11.2 g of KOH are present in $(11.2 \times 1000)/5.6$

$= 2000$ ml of 0.1 *M* KOH solution

7. The mass of 0.1 *M* KOH solution required to neutralize the acid is $m = 2000$ ml $\times$ 1.05 g/ml $= 2100$ g.

Example 4. On passing 10 litres of a gaseous mixture of nitrogen dioxide and nitrogen (measured at STP) through a sodium hydroxide solution, a mixture of sodium nitrite and sodium nitrate is formed. A mass of 6.32 g of potassium permanganate is required to oxidize the above sodium nitrite in a sulphuric acid medium, sodium nitrate and manganous sulphate being the products of this reaction. Determine the mass percents of the components of the gaseous mixture.

Solution. 1. First, let us write the equations for the reactions taking into account that N_2 does not react with NaOH:

$$2NO_2 + 2NaOH = NaNO_3 + NaNO_2 + H_2O$$

$$5NaNO_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5NaNO_3 + 3H_2O$$

2. The mass of sodium nitrite which is to be oxidized by 6.32 g of potassium permanganate may be calculated as follows:

2×158 g of $KMnO_4$ oxidize 5×69 g of $NaNO_2$

6.32 g of $KMnO_4$ oxidize $6.32 \times 5 \times 69/(2 \times 158)$

$= 6.9$ g of $NaNO_2$

3. The volume of NO_2, measured at STP, required to form 6.9 g of $NaNO_2$ is calculated from the first reaction:

69 g of $NaNO_2$ are formed from 44.8 litres of NO_2

6.9 g of $NaNO_2$ are formed from $6.9 \times 44.8/69$

$= 4.48$ litres of NO_2

Therefore, 10 litres of the given mixture contained 4.48 litres or 44.8% NO_2 and $100 - 44.8 = 55.2\%$ N_2.

PROBLEMS AND EXERCISES

1. What are the differences between the structures of a nitrogen and an oxygen molecule?

2. How would you account for the inertness of a nitrogen molecule?

3. How can you explain the fact that nitrogen has a highest oxidation state of +5 and a lowest of −3?

4. Why is nitrogen termed a "lifeless" gas?

5. Three flasks contain three different gases: nitrogen, oxygen, and carbon dioxide. How are they identified?

6. Why for large-scale fertilizer production nitrogen is generally converted into ammonia, rather than into nitrogen(II) oxide?

7. How can nitrogen get into the soil in nature?

8. Why while reacting with water or an acid ammonia actively accepts proton from them?

9. How does the combustion of ammonia in oxygen differ from its catalytic oxidation? What catalyst is used in this case?

10. How can nitrogen be purified from such impurities as ammonia, oxygen, or carbon dioxide?

11. Why can concentrated sulphuric acid not be employed for drying ammonia?

12. Will the electrical conductivity of water change when the following gases pass through it: (a) nitrogen(II) oxide, (b) ammonia, and (c) nitrogen dioxide?

13. Give examples of reactions in which nitrogen changes its oxidation state (a) from +4 to +5, (b) from +5 to +4, and (c) from −3 to +2.

14. In which cases is nitric acid reduced while reacting with metals: (a) concentrated nitric acid is reduced to

N_2O and NO_2, (b) dilute nitric acid is reduced to NH_3 and NO?

15. Which types of salts can nitric acid form? How can nitrates be distinguished chemically?

16. In which cases heating of ammonium salts results in the evolution of (a) ammonia, (b) nitrogen(I) oxide, and (c) nitrogen?

17. It is well known that all nitrates decompose on heating. In which case one can expect the formation of (a) another salt, (b) a metal oxide, and (c) a metal?

18. Write the equations for the reactions between nitrogen and each of potassium, zinc, and aluminium.

19. What reactions would you employ to purify nitrogen from the impurities of oxygen, chlorine or hydrogen sulphide?

20. Three different cylinders are filled with nitrogen, ammonia, and nitrogen(I) oxide, respectively. How can these gases be identified?

21. Write the equations for the reactions of preparation of ammonium sulphate from nitrogen, oxygen, hydrogen, sulphur and water.

22. Write the equations for the synthesis of ammonium nitrate from nitrogen, hydrogen, oxygen and water.

23. Write the equations in molecular and ionic forms for the reactions between sulphuric acid and each of ammonia, ammonium hydroxide, and lead(II) nitrate.

24. When 3.648 g of magnesium react with nitrogen, 5.048 g of magnesium nitride are formed. What is the formula of the nitride?

25. Ammonia obtained by reacting 1.12 litres of nitrogen, measured at STP, with an excess hydrogen was passed through 28.7 ml of 25% NH_4OH solution with a density of 0.907 g/ml. Determine the percent strength of the new solution.

26. To an aqueous ammonia solution was added an equivalent amount of aluminium sulphate. Taking account of the fact that the sulphate salt is hydrolyzed, predict whether the solution will be acidic, basic or neutral.

27. How many litres of nitric acid solution containing 48 mass percent of HNO_3 may be obtained from 44.8 litres of ammonia, measured at STP?

28. Calculate the molar concentration of a nitric acid solution with a density of 1.4 g/ml and containing 65% by mass of HNO_3.

29. Determine the percent strength of nitric acid, if 1 litre of water is added to 500 ml of 32% HNO_3 solution of density 1.2 g/ml.

30. What volume of 30% HNO_3 solution with a density of 1.18 g/ml will be required to dissolve 10 g of an alloy containing 60% by mass of copper and 40% of silver?

31. Write the molecular and ionic equations for the reactions between concentrated nitric acid and each of silver, magnesium and barium.

32. Write the molecular and ionic equations to represent the reactions that occur between dilute nitric acid and each of potassium, zinc and lead.

33. Write the molecular and ionic equations for the reactions between concentrated nitric acid and each of carbon, sulphur and phosphorus.

34. Write the molecular and ionic equations to represent the reactions occurring between dilute nitric acid and each of bromine, carbon and sulphur.

35. Set up the equations for reactions and mention the conditions under which the following conversions may be carried out:

(a) $\overset{0}{N} \rightarrow \overset{+2}{N} \rightarrow \overset{+4}{N} \rightarrow \overset{+5}{N}$ and (b) $\overset{0}{N} \rightarrow \overset{-3}{N} \rightarrow \overset{+2}{N} \rightarrow \overset{+4}{N}$

36. Set up the equations for reactions and mention the conditions under which the following transformations may be carried out:

(a) $\overset{+4}{N} \rightarrow \overset{+5}{N} \rightarrow \overset{+2}{N} \rightarrow \overset{+4}{N}$ and (b) $\overset{+5}{N} \rightarrow \overset{-3}{N} \rightarrow \overset{0}{N} \rightarrow \overset{+2}{N}$

37. Write the equations for reactions with the help of which one may carry out the following conversions:

(a) $NH_4OH \rightarrow (NH_4)_2SO_4 \rightarrow NH_3 \rightarrow NO$ and

(b) $NH_3 \rightarrow NH_4NO_2 \rightarrow N_2 \rightarrow NO$

38. Write the equations for reactions used to carry out the following transformations:

(a) $NaNO_3 \rightarrow O_2 \rightarrow NO_2 \rightarrow HNO_3 \rightarrow Fe(NO_3)_3$

(b) $Cu(NO_3)_2 \rightarrow NO_2 \rightarrow HNO_3 \rightarrow Hg(NO_3)_2 \rightarrow NO_2$

39. Write the equations in molecular and ionic forms for reactions with the aid of which the following transformations may be carried out:

(a) $N_2O_5 \rightarrow KNO_3 \rightarrow HNO_3 \rightarrow Cu(NO_3)_2 \rightarrow NO_2$

(b) $HNO_3 \rightarrow Fe(NO_3)_3 \rightarrow Al(NO_3)_3 \rightarrow NaAlO_2 \rightarrow Al(NO_3)_3$

40. Write the equations for decomposition of the following ammonium salts: $(NH_4)_2CO_3$, NH_4NO_2, NH_4NO_3, NH_4Cl and $NH_4H_2PO_4$.

41. Complete the following reactions, write the electronic equations (half-reactions) and determine the oxidizing and reducing agents:

(a) $HNO_2 + Br_2 + H_2O \rightarrow HNO_3 + HBr$

(b) $FeS_2 + HNO_3 \rightarrow Fe(NO_3)_3 + NO + H_2SO_4$

42. The degree of dissociation of a 1 *M* potassium nitrate solution equals 70%. How many grams of electrolyte dissociate into ions?

43. What volume, measured at STP, will occupy gases which are formed when 1 kg of potassium nitrate is exploded in a mixture of carbon and sulphur according to the following equation?

$$2KNO_3 + 3C + S = K_2S + 3CO_2 + N_2$$

44. How much ammonium nitrate will be required in order to yield a volume of 2 litres of nitrogen(I) oxide measured at STP?

45. Calculate the mass of sodium nitrate required to prepare 200 kg of a nitric acid solution containing 20% by mass of HNO_3.

46. Which of the following salts undergo hydrolysis: $NaNO_3$, NH_4NO_3, $Cu(NO_3)_2$, KNO_2, $Ba(NO_2)_2$? Write the equations for hydrolysis in molecular and ionic forms.

47*. Nitrogen dioxide obtained by decomposing 3.31 g of lead(II) nitrate was passed through 7.76 litres of a potassium hydroxide solution with a density of 1.288 g/ml and containing 30% by mass of KOH. Determine the mass percent of the substance in the solution thus obtained.

48. 5.95 g of a mixture of zinc and zinc oxide reacted with sodium hydroxide to liberate 1.12 litres of a gas

measured at STP. How many millilitres of nitric acid with a density of 1.14 g/ml and containing 20% by mass of HNO_3 will be required to dissolve the mixture of zinc and zinc oxide, if it is known that zinc liberates ammonia from the given nitric acid?

49*. A volume of 89.6 litres of a mixture of nitrogen and hydrogen, measured at STP, is passed through a catalyst resulting thereby in a volume of 67.2 litres of a mixture of gases. Ammonia thus obtained is dissolved in a volume of 100.88 ml of an ammonia solution with a density of 0.95 g/ml and containing 12% by mass of NH_4OH. Calculate the percent strength of the final solution.

50. Determine the mass percent of ammonia in a solution obtained by diluting 1 litre of 25% aqueous ammonia solution having a density of 0.9 g/ml with 9.1 litres of water. How many grams of ferric hydroxide can be precipitated by 5 g of the final solution?

51*. On passing a mixture of gases, formed after nitric acid decomposition, through a volume of 212.1 ml of 12% KOH solution with a density of 1.1 g/ml the alkali solution was completely neutralized. What volume of 63% HNO_3 solution with a density of 1.43 g/ml was decomposed? How much copper may be dissolved in this volume of acid?

52*. Hydrogen sulphide was passed through a solution containing 28.2 g of cupric nitrate and 33.1 g of lead nitrate until complete precipitation of the metal sulphides. Determine the volume of hydrogen sulphide measured at STP which was consumed for precipitation and the mass percents of the metal sulphides thus formed.

53*. A mass of 2 g of technical-grade copper was dissolved in nitric acid. The solution thus obtained was treated with an alkali. The calcination of the precipitate thus formed yielded a mass of 2.4 g of cupric oxide. What is the volume (at STP) of nitric oxide evolved on calcination? How many millilitres of a nitric acid solution containing 20% by mass of HNO_3 and having a density of 1.12 g/ml entered into the reaction? Determine the mass percent of copper in the technical-grade sample.

54*. The yield of ammonia obtained from 56 litres of a mixture of nitrogen and hydrogen is 40%. It was then

absorbed by 92.04 g of a phosphoric acid solution. Determine the percent strength of phosphoric acid and the composition of the ammonium salt, if it is known that by treating the latter with a silver acetate solution, 104.8 g of a precipitate are formed.

55*. When 100 ml of ammonia were decomposed to elemental state, the volume increased by 50 ml. Determine the mass percent of ammonia decomposed and the percent strength of the ammonia solution formed by dissolving the undecomposed ammonia in 100 ml of water.

56. Determine the mass percents of potassium and of nitrogen in the following fertilizers: (a) potassium nitrate and (b) ammonium nitrate.

57. What is the mass of sodium nitrate which contains the same mass of nitrogen as a mass of 25.25 g of potassium nitrate does?

58. How many times is ammonia heavier than hydrogen? How many times is the former lighter than nitrogen?

59. How many molecules of nitrogen are there in 896 ml of the gas measured at STP?

60. How many moles and how many molecules are there in 460 g of nitrogen dioxide?

61. Express both in moles and in grams 3×10^{23} molecules of nitric oxide.

62. 250 ml of a nitric acid solution with a density of 1.3 g/ml were diluted with 1 litre of water. Calculate the percent strength and the molar concentration of the final solution.

63. What volumes at STP will occupy a mass of 560 g of nitrogen gas and a mass of 25.5 g of ammonia gas?

64. How many litres of oxygen are required for complete oxidation of 500 litres of ammonia?

65. Assuming that air contains 78% nitrogen, how many litres of nitrogen may be obtained at STP from 1 m^3 of air?

66. 10 g of ammonia were mixed with 10 g of hydrogen chloride. Which of the gases was taken in excess and what is the mass of the unreacted gas?

67. How much ammonia will be required to prepare 100 kg of nitric acid, if the production loss is 5%?

68. What volume of ammonia measured at STP is required to obtain 264 g of ammonium sulphate?

69. 48 kg of ammonia are obtained from 56 kg of nitrogen. What is the yield of ammonia in mass percent with respect to the theoretical yield?

70. Oxidation of 17 kg of ammonia yielded 27 kg of nitric oxide. Calculate the yield of nitric oxide in mass percent with respect to the theoretical yield.

71. 5.1 g of ammonia were mixed with 12 g of hydrogen chloride. Which substance and in what amount was formed?

72. The yield of ammonia in mass percent with respect to the theoretical yield constitutes 90%. Calculate the mass of ammonia obtained by reacting 214 g of ammonium chloride with an excess calcium hydroxide.

73. How many kilograms of 80% H_2SO_4 solution are required to prepare ammonium sulphate from 51 kg of ammonia?

74. How many grams of a nitric acid solution containing (a) 90% and (b) 35% by mass of HNO_3 are required in order to dissolve 32 g of copper?

75. 6.25 g of a mixture of potassium and sodium carbonates are required to neutralize 200 ml of 0.5 *M* nitric acid solution. Determine the composition of the mixture.

76. Assuming the production loss for ammonia to be 3%, calculate how many kilograms of ammonia are required to prepare 500 kg of nitric acid containing 60% by mass of HNO_3.

77. What mass of nitric acid will be obtained when sulphuric acid reacts with 1 ton of saltpeter containing 95% sodium nitrate, assuming the production loss to be 2%?

78. One kilogram of (a) sodium ($NaNO_3$) and (b) potassium (KNO_3) saltpeter was taken for the preparation of nitric acid. How much acid containing 60% by mass of HNO_3 may be obtained in each case?

79. How many litres of 2 *M* solution may be obtained from 500 ml of a nitric acid solution having a density of 1.41 g/ml and containing 68% by mass of HNO_3?

80. How many cubic metres of ammonia (measured at STP), and how many kilograms of a nitric acid solution

containing 50% by mass of HNO_3 will be required to prepare 50 kg of ammonium saltpeter containing 97.5% by mass of ammonium nitrate?

3.2 PHOSPHORUS AND ITS COMPOUNDS

Unlike nitrogen, phosphorus is an active nonmetal. In the elemental form it exists in several modifications—white, red and black. The white modification is the most reactive. It readily reacts with simple substances. With oxygen it forms two oxides, P_2O_3 and P_2O_5, which are acidic in nature. The corresponding acid of phosphorus pentoxide, P_2O_5, is orthophosphoric acid, H_3PO_4. Salts of this acid are called orthophosphates. H_3PO_4 does not exhibit oxidizing properties, is tribasic, moderately weak acid and forms neutral salts like orthophosphates and acid salts such as hydrogen orthophosphates and dihydrogen orthophosphates.

Example 1. Write down the equations for the reactions which occur when the following transformations are carried out:

$$Ca_3(PO_4)_2 \rightarrow P \rightarrow H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \rightarrow CaHPO_4$$

Also, mention the reaction conditions.

Solution. 1. Phosphorus is prepared by reducing calcium phosphate, contained in apatite and phosphorite, with coke and sand in an electric furnace according to the following equation:

$$Ca_3(PO_4)_2 + 5C + 3SiO_2 = 3CaSiO_3 + 5CO + 2P$$

2. Strong oxidizing agents such as nitric and concentrated sulphuric acids oxidize phosphorus to orthophosphoric acid:

$$P + 5HNO_3\ (conc.) = H_3PO_4 + 5NO_2 + H_2O$$

3. Calcium dihydrogen phosphate (double superphosphate) may be prepared by treating phosphorite or apatite containing calcium phosphate with phosphoric acid:

$$4H_3PO_4 + Ca_3(PO_4)_2 = 3Ca(H_2PO_4)_2$$

4. Calcium hydrogen phosphate, $CaHPO_4$ (also called precipitate) can be prepared by treating calcium dihydro-

gen phosphate with alkali metal hydrogen phosphates:

$$Ca(H_2PO_4)_2 + K_2HPO_4 = CaHPO_4 + 2KH_2PO_4$$

Calcium hydrogen phosphate is sparingly soluble in water, while potassium dihydrogen phosphate is soluble in it.

Example 2. Technical-grade zinc phosphide contains metallic zinc as an impurity. A mixture of gases, phosphine and hydrogen, was obtained in 4:1 ratio when this phosphide was treated with hydrochloric acid. Determine the mass percent of metallic zinc in the technical-grade phosphide sample.

Solution. Hydrochloric acid reacts with zinc and zinc phosphide according to the following equations:

$$Zn + 2HCl = ZnCl_2 + H_2$$

$$Zn_3P_2 + 6HCl = 3ZnCl_2 + 2PH_3$$

It follows from these two equations that when the mole ratio of Zn and Zn_3P_2 is 1:1, then the volume ratio of PH_3 and H_2 is 2:1, and when the volume ratio of PH_3 and H_2 is 4:1, then the mixture contains 2 moles of Zn_3P_2 ($M_r = 257$) per each mole of Zn ($A_r = 65$). That is, 65 g of Zn are present per each 514 g of Zn_3P_2. The mass of the mixture will, therefore, be 514 + 65 = 579 g and the mass percent of zinc in the sample may be calculated as follows:

579 g correspond to 100%

65 g correspond to (65 g × 100%)/579 g = 10.9%

Example 3. Calcium phosphide formed by reacting calcium orthophosphate with magnesium was hydrolyzed by water. The evolved phosphine was burnt in air to yield phosphorus pentoxide. How many litres of air, containing 21% by volume of oxygen, were required to burn phosphine and how many grams of magnesium metaphosphate would be obtained, if 2.4 g of magnesium were used for reducing calcium phosphide and the volumes of the gases were measured at STP?

Solution. The equations for the involved reactions are:

$$Ca_3(PO_4)_2 + 8Mg = Ca_3P_2 + 8MgO \quad (1)$$

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3 \quad (2)$$

$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O \quad (3)$$

$$MgO + P_2O_5 = Mg(PO_3)_2 \quad (4)$$

It follows from the first equation that

8×24 g of Mg yield 8×40 g of MgO

2.4 g of Mg yield 2.4 g $\times 8 \times 40$ g/(8×24) g

$= 4$ g of MgO

and, 8×24 g of Mg yield 182 g of Ca_3P_2

2.4 g of Mg yield 2.4 g $\times$ 182 g/(8×24) g

$= 2.275$ g of Ca_3P_2

Since all reagents required for calculations react in equivalent proportions, we can determine from the second and third equations the volume of oxygen used for burning phosphine as follows:

182 g of Ca_3P_2 consume 4×22.4 litres of O_2

2.275 g of Ca_3P_2 consume 2.275 g $\times 4$

$\times$ 22.4 litres/182 g = 1.12 litres of O_2

So, the volume of air used may be calculated as

21 litres of O_2 are obtained from 100 litres of air

1.12 litres of O_2 are obtained from 1.12 litres

$\times$ 100 litres/21 litres = 5.33 litres of air

The mass of magnesium metaphosphate may be found from the fourth equation:

40g of MgO yield 182 g of $Mg(PO_3)_2$

4 g of MgO yield 4 g $\times$ 182 g/40 g = 18.2 g of $Mg(PO_3)_2$

PROBLEMS AND EXERCISES

1. Why does phosphorus not occur in nature in free state? In the form of which compounds it occurs in nature?

2. On the basis of the position of phosphorus in the periodic table: (a) write the formulas for phosphorus oxide and hydroxide, (b) mention the type of crystal lattice

for phosphorus, and (c) name the acids which may be formed from the acidic oxides of phosphorus.

3. How does the crystal lattice of white phosphorus differ from those of red and black phosphorus? How does this influence the chemical properties of the allotropic modifications of phosphorus?

4. What are the oxidation numbers of phosphorus in HPO_3, H_3PO_4, $H_4P_2O_7$, PH_4Cl, Ba_3P_2, PH_3, P_2O_5, PCl_5 and K_3PO_4?

5. What are the similarities between phosphorus and sulphur in terms of (a) the structure of atoms and (b) the nature of oxides formed by them?

6. What are the differences between phosphorus and nitrogen in terms of (a) the structure of atoms and (b) the nature of their oxides?

7. What is superphosphate and how is it prepared? How does it differ from double superphosphate? Why is it that the latter salt is a better soil fertilizer?

8. Why is phosphorite powder generally used for soil with increased acidity, whilst superphosphate for any soil? How would you distinguish between them experimentally?

9. What reactions occur when each of the following fertilizers is introduced into acidic soil: (a) phosphorite powder, (b) dolomite powder, $CaCO_3 \cdot MgCO_3$, (c) limestone? State whether in all of these cases a reduction in soil acidity may be attained.

10. How can you prepare white, red and black phosphorus?

11. Where are the phosphorus compounds used?

12. Determine the oxidation numbers of phosphorus and the types of chemical bonds in Na_3P, PH_3, KPO_3 and P_2O_5.

13. The oxide of a pentavalent element contains 56.33% by mass of oxygen. Calculate the atomic mass of the element.

14. Determine the molecular formula of one of the phosphorus oxides which contains 56.4% by mass of phosphorus. The vapour density of this oxide with respect to air equals 7.7.

15. How much each of calcium phosphate, coal and sand will be required in order to prepare 1 kg of phosphorus?

16. With which of the following substances may phosphorus pentoxide react: (a) water, (b) calcium oxide, (c) nitric acid, (d) sodium hydroxide, and (e) coal? Write the equations for the possible reactions.

17. Volatile phosphorus hydrides may be prepared by the action of hydrochloric acid on phosphides or of an alkali on phosphonium chloride (an analogue of ammonium chloride). Write the equations for these reactions.

18. How can orthophosphoric acid be prepared starting from (a) elemental phosphorus? (b) phosphorus pentoxide? (c) calcium phosphate?

19. With which of the following substances may orthophosphoric acid react: (a) silver, (b) zinc oxide, (c) barium chloride, (d) calcium hydroxide, and (e) sulphur trioxide? Write the ionic equations for the reactions where possible.

20*. Phosphorus pentoxide formed by burning 15.5 g of phosphorus in oxygen was dissolved in 500 ml of water. The solution thus formed was mixed with 12.32 ml of a calcium hydroxide solution having a density of 1 g/ml and containing 0.15% by mass of $Ca(OH)_2$. Determine the composition of the isolated salt and its mass percent in the solution.

21. Determine the percent strength of 9 *M* phosphoric acid solution which has a density of 1.15 g/ml.

22*. 14.2 g of phosphorus pentoxide were dissolved in 500 ml of a phosphoric acid solution having a density of 1.2 g/ml and containing 28% by mass of H_3PO_4. Determine the percent strength of the new solution.

23. How many grams of calcium hydroxide will enter into a reaction with phosphoric acid, if 43 g of precipitate are formed?

24*. 40 g of a mixture of copper, calcium and zinc were treated with phosphoric acid. This resulted in the liberation of 13.44 litres of hydrogen measured at STP. When the same amount of mixture was reacted with 20 g of 40% sodium hydroxide solution, 2.24 litres of a gas measured at STP were liberated. Determine the mass percent of the mixture.

25. How many grams of disubstituted calcium phosphate are formed when 13.72 g of orthophosphoric acid react with 74 g of calcium hydroxide?

26. How much phosphorite and how much sulphuric acid (density 1.73 g/ml) containing, respectively, 90% and 80% by mass of calcium phosphate and H_2SO_4 are required in order to prepare 1 ton of ordinary superphosphate?

27*. Phosphorus pentoxide formed by oxidizing 6.2 g of phosphorus was all dissolved in 25 ml of a sodium hydroxide solution having a density of 1.28 g/ml and containing 25% by mass of NaOH. Determine the composition of the produced salt of orthophosphoric acid and its mass percent in the solution.

28*. Phosphorus pentoxide prepared by oxidizing 6.2 g of phosphorus was dissolved in 23.6 ml of a KOH solution having a density of 1.19 g/ml and containing 20% by mass of KOH. What are the composition and the mass percent of the salt formed as a result of dissolution?

29*. 2.24 litres of ammonia measured at STP are passed through 115 g of an ammonium dihydrogen phosphate solution containing 10% by mass of $(NH_4)H_2PO_4$. Which salt and in what amount will be produced?

30. Write the molecular and ionic equations for the reactions between (a) ammonium hydrogen phosphate and calcium hydroxide, (b) barium dihydrogen phosphate and barium hydroxide, and (c) potassium hydrogen phosphate and sodium hydroxide.

31. With which of the below-listed substances can calcium phosphate react: (a) sulphuric acid, (b) orthophosphoric acid, (c) sodium nitrate, (d) potassium hydroxide? Write the ionic equations for the possible reactions.

32. Write the formulas of magnesium metaphosphate, calcium orthophosphate, and barium pyrophosphate. What is the basicity of the acids from which the above salts are formed?

33. How will you prepare double superphosphate starting from phosphorite and sulphuric acid? Write the ionic equations to represent the involved reactions.

34. A sample of a phosphorus fertilizer contains 60% $CaHPO_4$ and 40% $CaHPO_4 \cdot 2H_2O$. Calculate the mass percent of phosphorus in this fertilizer.

35. State whether each of the following salts will give an acidic, a basic or a neutral solution with water:

K_3PO_4, K_2HPO_4 and KH_2PO_4. Write the net and complete ionic equations for the salt hydrolysis.

36. Derive the simplest formulas for three phosphorus sulphides, if they contain, respectively, 43.6, 62.6 and 72% sulphur.

37. Write the molecular equations for reactions which correspond to the following ionic equations:

(a) $Ca_3(PO_4)_2 + 4H^+ \rightarrow 3Ca^{2+} + 2H_2PO_4^-$

(b) $Ca_3P_2 + 6H^+ \rightarrow 2PH_3 + 3Ca^{2+}$

(c) $PO_4^{3-} + 3H^+ + 2OH^- \rightarrow HPO_4^{2-} + 2H_2O$

38. How would you carry out the following transformations:

(a) $\overset{+5}{P} \rightarrow \overset{0}{P} \rightarrow \overset{+5}{P}$, (b) $\overset{0}{P} \rightarrow \overset{+3}{P} \rightarrow \overset{+5}{P}$, (c) $\overset{+5}{P} \rightarrow \overset{0}{P} \rightarrow \overset{-3}{P}$

39. Which reactions occur when the following conversions are carried out:

(a) $P \rightarrow P_2O_5 \rightarrow H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \rightarrow Ca_3(PO_4)_2 \rightarrow P$

(b) $P \rightarrow H_3PO_4 \rightarrow NaH_2PO_4 \rightarrow Na(NH_4)_2PO_4 \rightarrow Ca_3(PO_4)_2 \rightarrow Ca(H_2PO_4)_2$

40. Using the ion-electron method put the corresponding coefficients in the following redox reactions:

(a) $P + CuSO_4 + H_2O \rightarrow H_3PO_4 + Cu + H_2SO_4$

(b) $P + H_2SO_4 \rightarrow H_3PO_4 + SO_2 + H_2O$

41. The mineral phosphorite contains 28% by mass of phosphorus pentoxide. Determine the mass percent of impurity in the given phosphorite sample.

42. Determine the mass of calcium hydrogen phosphate, $CaHPO_4$ which contains as much phosphorus as 1 kg of $(NH_4)_2HPO_4$ does.

43. How much phosphorite containing 60% by mass of $Ca_3(PO_4)_2$ is required in order to prepare 10 kg of phosphorus, assuming the production loss to be 5%?

44. How much calcium hydroxide containing 80% by mass of $Ca(OH)_2$ is required in order to prepare 10 kg of precipitate?

45. How much phosphorite containing 70% by mass of $Ca_3(PO_4)_2$ is required to prepare double superphosphate containing 500 kg of $Ca(H_2PO_4)_2$?

46. Calculate the yield of phosphorus in mass percent with respect to the theoretical yield when 24.8 kg of phosphorus are obtained from 155 kg of calcium phosphate.

47. How much diammophos (ammonium dihydrogen orthophosphate) can be obtained by reacting ammonia with 10 tons of phosphoric acid?

48. Calculate the mass of orthophosphoric acid which can be obtained by reacting 77.5 kg of calcium orthophosphate with 120 kg of sulphuric acid.

49. What is the mass of phosphorus pentoxide in 10 kg of phosphorite containing 60% by mass of $Ca_3(PO_4)_2$?

50. How many grams of phosphorus pentoxide are formed on burning 93 g of phosphorus?

51. One mole of a potassium phosphate solution is mixed with one mole of a potassium dihydrogen phosphate solution. Determine the composition of the salt obtained by evaporating the mixed solution.

52. What will be the concentration of the orthophosphoric acid solution obtained by dissolving 35.5 g of P_2O_5 in 800 g of an H_3PO_4 solution containing 25% by mass of H_3PO_4?

53. What mass percent of $CaHPO_4 \cdot 2H_2O$ is lost when calcined?

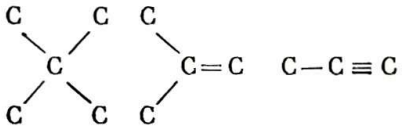
4
GROUP IVA ELEMENTS

The elements carbon (C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb) constitute Group IVA of the periodic table. They form the carbon family of elements. Each of these elements has four electrons in the outermost shell of their atoms. The atoms of these elements could, therefore, accept or donate four electrons each, exhibiting thereby the oxidation numbers of -4 and $+4$, respectively. However, as the sizes of the atoms increase within the Group from carbon to lead, the nonmetallic properties decrease, while the metallic ones increase. Germanium exhibits both nonmetallic and metallic properties. Tin and lead are typical metals. The oxidation numbers of -4 and $+4$ are characteristic of

nonmetals carbon and silicon alone. They exhibit the maximum valence of four with respect to both hydrogen and oxygen. In addition, they can form a few unstable compounds with the oxidation number of +2 (oxides, sulphides).

Tin and lead, on the other hand, form stable bivalent compounds which are even more stable than those with a valence of four. Moreover, tin and lead can exist in the form of positive ions or cations.

An important feature of a few elements in Group IVA is their ability to form covalent bonds between similar atoms. This feature is especially characteristic of carbon atoms, as a result of which various types of chains are formed:



For germanium atoms this property is less characteristic.

4.1 CARBON AND ITS COMPOUNDS

In the free state, carbon is chemically inert. As simple substance it can exist in the form of four modifications, viz. diamond, graphite, amorphous carbon, and polymer, carbon or Carbyne. With oxygen, carbon forms two oxides. These are carbon monoxide, CO, and carbon dioxide CO_2. The first oxide is nonsalt-forming, whilst the second one is acidic in nature. The corresponding acid of carbon dioxide is carbonic acid. This is a weak, dibasic acid, which can form two types of salts: neutral (called carbonates) and acid salts (called bicarbonates).

Example 1. Which reactions correspond to the following transformations:

$$C \rightarrow CH_4 \rightarrow CO \rightarrow CO_2 \rightarrow BaCO_3 \rightarrow Ba(HCO_3)_2 \rightarrow BaCO_3 \rightarrow CO_2$$

Write the ionic equations where possible.

Solution.

1. $C + 2H_2 \xrightarrow{Ni,\ t} CH_4$ (on a nickel catalyst)
2. $CH_4 + H_2O(g) \xrightleftharpoons{t} CO + 3H_2$
3. $2CO + O_2 \xrightleftharpoons{t} 2CO_2$
4. $CO_2 + Ba(OH)_2 = BaCO_3 + H_2O$
   $CO_2 + Ba^{2+} + 2OH^- = BaCO_3 + H_2O$
5. $BaCO_3 + H_2O + CO_2 = Ba(HCO_3)_2$
   $BaCO_3 + H_2O + CO_2 = Ba^{2+} + 2HCO_3^-$
6. $Ba(HCO_3)_2 \xrightleftharpoons{t} BaCO_3 + H_2O + CO_2$
7. $BaCO_3 \xrightleftharpoons{t} BaO + CO_2$

Example 2. With which of the following substances will carbon monoxide react: H_2, CuO, O_2, CO_2, NaOH, HCl, Cl_2, and H_2O?

Solution. 1. At high temperatures carbon monoxide reacts with hydrogen in the presence of nickel catalyst to yield methyl alcohol:

$$2H_2 + CO = CH_3OH$$

2. CO exhibits strong oxidizing properties:

$$CuO + CO = Cu + CO_2$$

3. CO burns in oxygen in blue flame forming CO_2:

$$O_2 + 2CO = 2CO_2$$

4. Under ordinary conditions CO is a nonsalt-forming oxide. At an elevated temperature (200 °C) and pressure (506.15 kPa), however, it behaves as an acidic oxide, thus forming formates with alkalies:

$$NaOH + CO = HCOONa \text{ (sodium formate)}$$

5. In the presence of a catalyst, CO reacts with Cl_2 to yield a colourless poisonous gas phosgene:

$$Cl_2 + CO = COCl_2$$

Carbon monoxide does not react with CO_2, HCl and H_2O.

Example 3. 1 litre of oxygen was added to 1 litre of a mixture of carbon monoxide and carbon dioxide. When the whole mixture was burnt, its volume decreased to

1.8 litres. Determine the volume percent of carbon monoxide and carbon dioxide in the mixture.

Solution. 1. The total volume of the mixture is 1 + 1 = 2 litres.

2. Let us write down the equation for the reaction of burning of carbon monoxide alone, since carbon dioxide does not react with oxygen:

$$2CO + O_2 = 2CO_2$$

3. As a result of the burning process, the volume of the mixture reduced by 0.2 litre, i.e. 2 litres — 1.8 litres = 0.2 litre (due to participation of oxygen in the burning process).

4. To burn carbon monoxide, 1 volume of O_2 is required for each 2 volumes of CO. This means that 0.2 litre of O_2 will be required for 0.4 litre of CO.

5. Now we can determine the volume percent of the mixture of gases in the following way:

1 litre of mixture corresponds to 100%

0.4 litre of CO corresponds to

(0.4 litre × 100%)/1 litre = 40%

Hence the given mixture contains 40% CO, 60% CO_2.

Example 4. Determine the masses of crystalline and anhydrous soda required to neutralize a mass of 24.5 kg of a sulphuric acid solution containing 20% by mass of H_2SO_4. Which of the two types of soda, crystalline or anhydrous, is economically more favourable for use, if 1 kg each of crystalline and anhydrous soda costs, respectively, 4 and 6 copecks?

Solution. 1. Sulphuric acid reacts with crystalline and anhydrous soda, the latter two reagents taken separately, according to the following equations:

$$Na_2CO_3 \cdot 10H_2O + H_2SO_4 = Na_2SO_4 + CO_2 + 11H_2O \quad (1)$$

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O \quad (2)$$

$$M_r(Na_2CO_3 \cdot 10H_2O) = 286,\ M_r(Na_2CO_3) = 106,$$

$$m = wm_1 = 0.2 \times 24.5 = 4.9 \text{ kg}$$

2. It follows from Eq. (1) that

98 g of H_2SO_4 use up 286 g of $Na_2CO_3 \cdot 10H_2O$

4.9 kg of H_2SO_4 use up $4.9 \times 286/98 = 14.3$ kg of $Na_2CO_3 \cdot 10H_2O$

Likewise, from Eq. (2) it follows that

98 g of H_2SO_4 use up 106 g of Na_2CO_3

4.9 kg of H_2SO_4 use up $4.9 \times 106/98 = 5.3$ kg of Na_2CO_3

3. The cost of crystalline soda required to neutralize the sulphuric acid is 14.3 kg × 4 copeck/kg = 57 copecks, while that of anhydrous soda is 5.3 kg × 6 copeck/kg = 32 copecks. Hence, anhydrous soda is cheaper and, therefore, preferable for neutralization purposes.

Example 5. A mixture of iron(II) and lead(II) carbonates was calcined. As a result of this an amount of 0.9 mole of carbon dioxide was evolved. The mixture of metal oxides obtained by decomposing the above carbonates was treated with sulphuric acid which resulted in a mass of 151.6 g of a sulphate as precipitate. Determine the composition of the starting mixture of carbonates in grams and mass percents.

Solution. Upon calcination, carbonates yield metal oxides and carbon dioxide:

$$FeCO_3 = FeO + CO_2 \quad (1)$$

$$PbCO_3 = PbO + CO_2 \quad (2)$$

When the mixture of metal oxides is treated with sulphuric acid, the following reactions take place:

$$FeO + H_2SO_4 = FeSO_4 + H_2O \quad (3)$$

$$PbO + H_2SO_4 = PbSO_4\downarrow + H_2O \quad (4)$$

Eqs. (1) and (2) show that the carbonates yield 1 mole each of CO_2 and the respective metal oxide. Eqs. (3) and (4) inform us that 1 mole of metal oxide leads to 1 mole of the respective sulphate. Of the two sulphates, lead sulphate is insoluble in water.

The mass of the precipitate is 151.63 g, this corresponds to 0.5 mole of $PbSO_4$, which took part in the reaction. Hence, the mixture contained 0.5 mole of lead carbonate, because for the formation of 0.5 mole of $PbSO_4$, 0.5 mole of PbO obtained from $PbCO_3$ was required. The amount of CO_2 formed from $PbCO_3$ was also 0.5 mole. Then the amount of CO_2 evolved from $FeCO_3$ constitutes 0.9 mole—0.5 mole = 0.4 mole, which means that 0.4 mole of $FeCO_3$ was decomposed. Therefore, the masses of the

components in the carbonate mixture are:

for $PbCO_3$ 0.5 mole $\times$ 267 g/mole = 133.6 g

for $FeCO_3$ 0.4 mole $\times$ 166 g/mole = 46.4 g

Hence the total mass of the mixture is 133.6 g + 46.4 g = = 180 g. And, the mass percent composition of the mixture is

$$PbCO_3 = \frac{133.6 \text{ g} \times 100\%}{180 \text{ g}} = 74.2\%$$

$$FeCO_3 = \frac{46.4 \text{ g} \times 100\%}{180 \text{ g}} = 25.8\%$$

PROBLEMS AND EXERCISES

1. Atoms of which element, nitrogen or carbon, will accept electrons more readily and why?
2. While forming chemical bonds why do generally four electrons of a carbon atom take part in bond formation, though it has only two unpaired electrons in the *p* orbital?
3. What type of chemical bonding is characteristic of carbon compounds? Which electrons take part in the bond formation?
4. What allotropes are formed by elemental carbon? How do their structures differ from one another?
5. How do diamond and graphite differ in physical properties?
6. For demonstrating the chemical properties of carbon, coal is taken rather than other allotropes of carbon. Explain why.
7. Does carbon change after adsorbing substances? Why is it that diamond and graphite are practically unable to adsorb substances?
8. How are coke and carbon black prepared? Where are they used?
9. What is the physiological action of carbon monoxide? Where is it used?
10. By which chemical method can a mixture of carbon oxides be separated?
11. How would you account for the fact that the amount of carbon dioxide in the earth atmosphere is nearly constant?

12. State whether the solutions of sodium carbonate and sodium bicarbonate will exhibit acidic, neutral or basic media on hydrolysis.

13. What reaction for CO_3^{2-} ion is to be carried out for its identification?

14. Which carbon compounds are contained in (a) air, (b) rocks and (c) underground waters?

15. Why is sodium carbonate (soda) used for washing clothes?

16. Which of the following salts are soluble in hydrochloric acid and why: $Ba(NO_3)_2$, $BaCO_3$, and $BaSO_4$?

17. Write down the formulas of compounds formed by carbon and (a) chlorine, (b) sulphur, (c) magnesium, and (d) aluminium.

18. Write down the equations for reactions between coal and (a) carbon dioxide, (b) chromium oxide, (c) lead(II) oxide, and (d) tin dioxide.

19. With which of the following substances will carbon monoxide react: MgO, O_2, H_2, H_2SO_4, Cl_2, KOH and K_2S? Write the corresponding reaction equations.

20. With which of the following substances will carbon dioxide react: NH_3, NaOH, H_2O, C, SO_3, BaO, HCl and $CuSO_4$? Write the reaction equations.

21. Write the reaction equations for the following transformations:

(a) $CO \rightarrow CO_2 \rightarrow Na_2CO_3 \rightarrow CaCO_3$

(b) $CH_4 \rightarrow CO_2 \rightarrow MgCO_3 \rightarrow MgCl_2$

22. Write the equations for reactions involved in the following conversions:

(a) $CO_2 \rightarrow CO \rightarrow CO_2 \rightarrow CaCO_3$

(b) $CH_4 \rightarrow CO_2 \rightarrow CO \rightarrow Mg$

23. On burning 20 ml of a mixture of carbon oxides in excess oxygen, the total volume of the whole mixture decreased by 4 ml. What is the mass percent of carbon monoxide in the starting mixture?

24. A mixture of gases consisting of 3 litres of hydrogen, 1 litre of carbon monoxide, and 4 litres of oxygen was exploded in an eudiometer. Determine the mass percent of the gas mixture after the reaction is over, assuming all the substances to be in the gaseous state.

25*. 5 litres of a mixture of gases, measured at STP and consisting of carbon monoxide, carbon dioxide, and nitrogen, were passed through an excess lime water. After this 5 g of a precipitate were formed. The remaining mixture of gases was passed over hot ferric oxide to yield 5.6 g of iron. What is the mass percent of gases in the original mixture?

26. What is the mass of carbon in 50 tons of calcium carbonate?

27. Is it possible to completely reduce copper from 60 g of cupric oxide by heating the latter with 9 g of coal?

28. What volume of carbon monoxide measured at STP will be evolved by reacting carbon dioxide with 4 kg of red-hot coal?

29. What gases and in what amounts (measured at STP) are formed by reacting 36 g of carbon with water?

30. How many cubic metres of carbon dioxide measured at STP may be obtained from 1 ton of limestone containing 95% $CaCO_3$? What volume of 25% NH_4OH solution with a density of 0.9 g/ml will be required to absorb the whole of CO_2, supposing a normal salt to be formed as a result of absorption?

31. What salt and how many grams of it will be formed in a solution, if 1.12 litres of carbon dioxide are passed through 50 ml of a potassium hydroxide solution which has a density of 1.1 g/ml and contains 12% by mass of KOH?

32*. A mixture of nitrogen and carbon dioxide is passed through 24.5 ml of 40% sodium hydroxide solution of density 1.225 g/ml. The whole of caustic soda was converted into an acid salt, and the volume of the remaining nitrogen was 2.8 litres at STP. Determine the composition of the original gas mixture in volume percents.

33. How many grams of calcium carbonate will precipitate when hard water containing 68 g of calcium sulphate is treated with soda?

34. What is the mass percent of hydrogen chloride in water, if 50 g of the solution requires 5.3 g of sodium carbonate for complete neutralization?

35. Potassium carbonate and bicarbonate solutions become differently coloured when an alcoholic solution of

phenolphthalein is added. How would you account for this fact? Write the equations for the hydrolysis of these salts.

36. Taking into account that carbon is tetravalent, determine its oxidation numbers in CH_4, C_2H_4, CaC_2, HCOH, HCOOH, and CCl_4.

37. Put coefficients in the following redox equations using the ion-electron method:

(a) $CS_2 + H_2O \rightarrow CO_2 + H_2S$

(b) $C + H_2SO_4 \rightarrow CO_2 + SO_2 + H_2O$

(c) $CO + NH_3 \rightarrow H_2O + HCN$

38. Balance the following redox equations with the aid of the ion-electron method:

(a) $CS_2 + O_2 \rightarrow SO_2 + CO_2$

(b) $CH_4 + H_2O \rightarrow CO + H_2$

(c) $C + HNO_3 \rightarrow CO_2 + NO_2 + H_2O$

39. The crystal hydrate, $Na_2CO_3 \cdot xH_2O$, contains 62.94% by mass of water. Calculate the amount of water of crystallization in the crystal hydrate.

40. When 4.64 g of a mixture of sodium carbonate and bicarbonate were treated with sulphuric acid, 4.97 g of anhydrous sodium sulphate were yielded. Determine the mass percent of sodium carbonate in the mixture.

41*. 2.24 litres of carbon monoxide measured at STP reacted with 30 g of 20% NaOH solution at 200 °C and 505.15 kPa. Calculate the mass percents of the substances in the solution thus obtained and write the structural formula of sodium formate.

42. A mass of 20 g of sodium carbonate is dissolved in 1 litre of water. Determine the percent strength and molar concentration of the obtained solution, if the solution has a density of 1.02 g/ml.

43*. 60 g of marble were treated with 50 ml of a hydrochloric acid solution having a density of 1.1 g/ml and containing 20% by mass of HCl. The liberated gas was passed through 250 ml of 0.1 *M* calcium hydroxide solution. Which substance and in what mass is formed as a result of this reaction?

44. What volume of carbon dioxide measured at STP will be formed on decomposition of 0.5 kg of natural lime-

stone containing 92% by mass of calcium carbonate? What minimal volume (in ml) of 25% NH_4OH solution of density 0.9 g/ml will be required to absorb the whole of carbon dioxide?

45. Which reactions should be used for the following transformations:

$$CO_2 \rightarrow Ca(HCO_3)_2 \rightarrow CaCO_3 \rightarrow CaCl_2 \rightarrow Ca(NO_3)_2 \rightarrow CaCO_3 \rightarrow CO_2$$

46. With the aid of which reactions the following conversions may be carried out:

(a) $Ba(NO_3)_2 \rightarrow BaCO_3 \rightarrow BaCl_2 \rightarrow BaCO_3$

(b) $CaCO_3 \rightarrow CO_2 \rightarrow Na_2CO_3 \rightarrow NaHCO_3$

(c) $CH_4 \rightarrow CO_2 \rightarrow Ca(HCO_3)_2 \rightarrow CaCO_3 \rightarrow CaCl_2$

Write the molecular and ionic equations for reactions where possible.

47. Write the molecular equations for reactions expressed below by the following ionic equations:

(a) $CO_3^{2-} + 2H^+ = CO_2 + H_2O$

(b) $CaCO_3 + 2H^+ = Ca^{2+} + CO_2 + H_2O$

(c) $CO_2 + OH^- = HCO_3^-$

(d) $HCO_3^- + H^+ = H_2O + CO_2$

48. Write the molecular equations for reactions expressed by the following ionic equations:

(a) $Ca^{2+} + CO_3^{2-} = CaCO_3$

(b) $CO_3^{2-} + CO_2 + H_2O = 2HCO_3^-$

(c) $CO_2 + 2OH^- = CO_3^{2-} + H_2O$

(d) $H_2CO_3 + SiO_3^{2-} = H_2SiO_3 + CO_3^{2-}$

49*. A mixture of carbon monoxide and carbon dioxide gases is passed through 124.5 ml of a caustic soda solution having a density of 1.225 g/ml and containing 40% by mass of NaOH. As a result of this, the caustic soda is all converted to a neutral salt and the remaining carbon monoxide occupies a volume of 3 litres at STP. Calculate the mass percent of the salt formed in the solution.

50*. 1 litre of oxygen is mixed with 1 litre of a mixture of carbon monoxide and carbon dioxide. After burning the resultant mixture was found to have a volume of

1.8 litres. Determine the composition of the original mixture in volume percent. What is the minimum volume of 10% caustic soda solution having a density of 1.11 g/ml which will be required to liberate pure oxygen from the gas mixture obtained after burning?

51*. The total volume of a mixture of carbon monoxide and oxygen equals 200 ml. When carbon monoxide is all burnt in oxygen present in the mixture, a volume of 150 ml of a mixture of carbon dioxide and oxygen is obtained. Determine the volume composition of the original gas mixture. Which salt and in what mass will be obtained by passing the obtained CO_2 through 100 ml of 0.5 *M* sodium hydroxide solution?

52. How many moles and how many molecules are there in 220 g of carbon dioxide?

53. Express 6.02×10^{22} molecules of carbon monoxide in moles and grams.

54. A mineral contains 40% Ca, 12% C and 48% O. Derive the simplest formula for the mineral.

55. Deduce the true formulas for two hydrocarbons which have molecular masses of $M_1 = 26$ and $M_2 = 78$, the same simplest formula and contain 92.3% C and 7.7% H (both by masses).

56. What volume at STP will occupy each of 14 g of carbon monoxide and 33 g of carbon dioxide?

57. A gas mixture consisting of CO_2 and O_2 has a density of 19 with respect to hydrogen. Calculate the volume composition of this mixture.

58. How many litres of carbon dioxide measured at STP may be obtained by burning 1 kg of coal containing 90% by mass of carbon?

59. Calculate the yield of carbon dioxide in mass percent with respect to the theoretical amount, if 60 g of it were obtained by treating 150 g of calcium carbonate with an excess hydrochloric acid.

60. How much coal containing 95% by mass of carbon is required to prepare 1000 m^3 of water gas, if the loss is 3%?

61. How many litres of carbon dioxide can a fire extinguisher produce (at STP) which contains 20 litres of a sodium bicarbonate solution of density 1.05 g/ml containing 8% by mass of $NaHCO_3$?

62. Calculate the mass of carbon dioxide obtained on decomposition of 1 ton of limestone containing 10% by mass of impurities.

63. Calculate the mass of carbon dioxide which may be obtained by treating 100 g of marble containing 95% by mass of $CaCO_3$ with 200 g of 25% HCl solution.

64. Calculate the mass percent of $CaCO_3$ in natural limestone, if 60 g of it react with an excess hydrochloric acid to yield 22 g of carbon dioxide.

65. When fused, 30 kg of limestone reacted with silicon dioxide to afford 40 kg of calcium silicate. Calculate the mass percent of $CaCO_3$ in the limestone.

66. What volume of carbon dioxide may be prepared at STP from 168 g of sodium bicarbonate (a) by calcination and (b) by treating with an acid?

67. On heating 146 g of a mixture of sodium carbonate and bicarbonate, its mass reduced to 137 g. What is the mass percent of sodium carbonate in the mixture?

68. A mass of 16.4 g of a mixture of calcium carbonate and magnesium carbonate was treated with 0.18 mole of carbon dioxide. Determine the composition of the mixture.

69. When 4.9 litres of carbon dioxide are passed through a sodium hydroxide solution, 22.9 g of a mixture of sodium carbonate and bicarbonate are isolated. Calculate the composition of the mixture thus formed.

70. Calculate the number of molecules of water in the crystal hydrate of sodium carbonate, if 5.3 g of anhydrous salt is formed after calcination of 13.3 g of the crystal hydrate.

71. How many grams of Na_2CO_3 are there in 500 ml of 0.5 *M* solution?

72. How many grams of calcium carbonate can react with 50 ml of 2 *M* hydrochloric acid solution?

73. A volume of 50 ml of 1 *M* hydrochloric acid solution is used for dissolving 6 g of limestone. Calculate the mass percent of $CaCO_3$ in the limestone.

4.2 SILICON AND ITS COMPOUNDS

Silicon occurs in nature only in the form of compounds. These are various types of silicate and quartz, SiO_2. Under ordinary conditions silicon is inert enough. It reacts with other elements (except fluorine) on heating only. Silicon dioxide, SiO_2, is acidic in nature. Silicic acids, whose general formula is $nH_2O \cdot mSiO_2$, are the derivatives of silicon dioxide. They are sparingly soluble in water. Salts of these acids are known as silicates. Amongst the latter, only the alkali metal silicates are soluble in water.

Example 1. Write the molecular and ionic equations for reactions that occur when the following transformations are carried out:

$$\begin{array}{ccccccc} Si & \rightarrow & Mg_2Si & \rightarrow & SiH_4 & \rightarrow & SiO_2 \\ \downarrow & & & & & & \downarrow \\ SiO_2 & \rightarrow & Si & \rightarrow & Na_2SiO_3 & \rightarrow & CaSiO_3 \end{array}$$

Write the electronic equations (half-reactions) for the redox reactions.

Solution. 1. $Si + 2Mg \xrightarrow{\text{fusion}} Mg_2Si$

$$\begin{array}{l} \overset{0}{Si} + 4e^- \rightarrow \overset{-4}{Si} \quad \Big| \times 1 \\ \overset{0}{Mg} - 2e^- \rightarrow \overset{+2}{Mg} \quad \Big| \times 2 \end{array}$$

2. $Mg_2Si + 2H_2SO_4 = 2MgSO_4 + SiH_4\uparrow$

$Mg_2Si + 4H^+ = 2Mg^{2+} + SiH_4$

3. SiH_4 ignites spontaneously in air:

$$SiH_4 + 2O_2 = 2H_2O + SiO_2$$

$$\begin{array}{rl} \overset{-4}{Si} - 8e^- \rightarrow \overset{+4}{Si} & \Big| \times 1 \\ \overset{0}{O_2} + 4e^- \rightarrow \overset{-2}{2O} & \Big| \times 2 \end{array}$$

4. $Si + O_2 = SiO_2$

$$\begin{array}{rl} \overset{0}{Si} - 4e^- \rightarrow \overset{+4}{Si} & \Big| \times 1 \\ \overset{0}{O_2} + 4e^- \rightarrow \overset{-2}{2O} & \Big| \times 1 \end{array}$$

5. $SiO_2 + 2Mg = 2MgO + Si$

$$\begin{array}{rl} \overset{+4}{Si} + 4e^- \rightarrow \overset{0}{Si} & \Big| \times 1 \\ \overset{0}{Mg} - 2e^- \rightarrow \overset{+2}{Mg} & \Big| \times 2 \end{array}$$

6. $Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$

$$\overset{0}{Si} - 4e^- \rightarrow \overset{+4}{Si} \quad \times 1$$
$$2H^+ + 2e^- \rightarrow H_2 \quad \times 2$$

$Si + 2OH^- + H_2O = SiO_3^{2-} + 2H_2$

7. $Na_2SiO_3 + CaCl_2 = CaSiO_3 + 2NaCl$

$SiO_3^{2-} + Ca^{2+} = CaSiO_3$

8. $SiO_2 + Ca(OH)_2 = CaSiO_3 + H_2O$

$SiO_2 + 2OH^- + Ca^{2+} = CaSiO_3 + H_2O$

Example 2. When 2 g of a mixture of silicon and carbon are treated with a sodium hydroxide solution which has a density of 1.4 g/ml and contains 60% by mass of NaOH, 1.12 litres of a gas measured at STP are evolved. Determine the mass percent of carbon in the mixture. How many millilitres of sodium hydroxide solution were used for this purpose?

Solution. Silicon alone reacts with sodium hydroxide:

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$$

From this equation we can determine the masses of silicon and pure sodium hydroxide used in this reaction:

44.8 litres of H_2 correspond to 28 g of Si

1.12 litres of H_2 correspond to 1.12 litres

$\times$ 28 g/44.8 litres = 0.7 g of Si

Therefore, there were 1.3 g (2 g — 0.7 g) of carbon in the mixture.

Now, 2 g constitute 100%

1.3 g constitute (1.3 g $\times$ 100%)/2 g = 65% of carbon.

28 g of Si react with 80 g of NaOH

0.7 g of Si reacts with (0.7 g $\times$ 80 g)/28 g = 2 g of NaOH

60 g of NaOH are found in 100 g of 60% solution

2 g of NaOH are found in (2 g $\times$ 100 g)/60 g

= 3.3 g of 60% solution

Therefore, the volume of the solution, $V = 3.3/1.4 = 2.37$ ml.

Example 3. 24 g of silicon dioxide were heated with 28.8 g of magnesium. When the obtained product was

treated with hydrochloric acid, 6.72 litres of hydrogen measured at STP were collected. Determine the mass of isolated silicon.

Solution. Silicon dioxide reacts with magnesium as follows:

$$\underset{48}{2Mg} + \underset{60}{SiO_2} = \underset{}{2MgO} + \underset{28}{Si} \qquad (1)$$

The given mass ratio of silicon dioxide and magnesium shows that magnesium is in excess amount in the given mixture. According to the above equation

60 g of SiO_2 react with 48 g of Mg

24 g of SiO_2 react with (24 g × 48 g)/60 g

= 19.2 g of Mg

That is, 28.8—19.2 = 9.6 g of magnesium do not enter into a reaction with SiO_2. The excess magnesium can react with silicon, formed above, according to the following equation

$$2Mg + Si = Mg_2Si \qquad (2)$$

After heating, the mixture consists of magnesium, silicon, magnesium oxide and magnesium silicide which react with hydrochloric acid as follows:

$$Si + HCl \not\rightleftharpoons$$

$$MgO + 2HCl = MgCl_2 + H_2O$$

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$$

$$Mg + 2HCl = MgCl_2 + H_2$$

It is clear from these four equations that hydrogen is liberated only when magnesium reacts with hydrochloric acid. Let us now calculate the mass of magnesium [see Eq. (3) above] consumed by hydrochloric acid:

22.4 litres of H_2 come from 24 g of Mg

6.72 litres of H_2 come from (6.72 litres × 24 g)/22.4 litres = 7.2 g of Mg

This means that 9.6 — 7.2 = 2.4 g of magnesium entered into a reaction with silicon following Eq. (2). From this

equation now we can calculate the amount of silicon consumed for the formation of magnesium silicide:

48 g of Mg react with 28 g of Si

2.4 g of Mg react with (2.4 g × 28 g)/48 g = 1.4 g of Si

But the yield of silicon from 24 g of SiO_2 is 11.2 g, which is found from Eq. (1) as follows:

60 g of SiO_2 yield 28 g of Si

24 g of SiO_2 yield (24 g × 28 g)/60 g = 11.2 g of Si

Hence, the mass of silicon left after magnesium silicide has been formed equals 11.2 g — 1.4 g = 9.8 g.

PROBLEMS AND EXERCISES

1. Write the electronic configuration of a silicon atom on the basis of its position in Mendeleev's periodic table. What are the oxidation numbers typical of it? In what do the properties of carbon and silicon resemble each other? In what differ?

2. In the form of which compounds does silicon occur in nature?

3. What type of oxides does silicon dioxide belong to? List its properties.

4. How will you prepare silicon dioxide from (a) water glass and (b) window glass?

5. How is a colloidal solution of silicic acid prepared in the laboratory?

6. Which precipitate is formed when ammonium nitrate is added to sodium silicate?

7. Write down the formulas of known silicon hydrides. In what do they resemble and in what differ from the carbon hydrides?

8. Why is it that the window glass loses its brightness and becomes dull over time? Account for this from the viewpoint of the chemical properties of glass.

9. Indicate the chemical composition of (a) carborundum, (b) glass, (c) kaolin, (d) water glass, (e) quartz and (f) cement.

10. Which potteries are used (a) in chemical industry, (b) in household, and (c) for construction purposes?

11. In what do the following systems differ: a suspension, a true solution and a colloidal solution?

12. What do the following dispersed systems represent: (a) a transparent dark brown liquid in which one can observe light scattering, (b) a green liquid in which, when a beam of light is passed through, "the path of the beam" is not visible, (c) a colourless liquid from which another colourless liquid rapidly rises to the surface, and (d) a white liquid from which a precipitate settles down? Which of these four cases corresponds to a colloidal solution?

13. Amorphous silicon is prepared by reducing quartz sand with magnesium. How will you isolate silicon from the mixture of solid substances obtained by the reduction? Write down the equations for the reactions involved.

14. Highly pure silicon used in semiconductor technology is prepared by decomposing silicon tetraiodide at high temperatures or by reducing silicon tetrachloride with zinc. Write the equations to represent these reactions.

15. Write down the equations for reactions between silicon and (a) hydrogen, (b) aluminium, (c) potassium hydroxide, and (d) hydrogen fluoride.

16. 10 g of a mixture of silicon and carbon were treated with 35.7 ml of a sodium hydroxide solution having a density of 1.4 g/ml and containing 40% by mass of NaOH. Determine the mass percents of the mixture components. What volume of gas measured at STP was liberated in this case?

17. How many millilitres of a sodium hydroxide solution having a density of 1.5 g/ml and containing 50% by mass of NaOH were used for dissolving 13 g of a mixture of silicon and sand, if the volume of the gas liberated as a result of this was 11.2 litres at STP?

18. Write down the equations for reactions between silicon and (a) calcium carbonate, (b) ferrous oxide, (c) coal, and (d) sodium hydroxide.

19. Complete the equations for the following reactions:

$SiO_2 + H_2O \rightarrow$ ..... $Si + O_2 \rightarrow$ ....

$SiO_2 + NaOH \rightarrow$ ..... $H_2SiO_3 + HCl \rightarrow$ ...

$SiO_2 + HNO_3 \rightarrow$ .... $Si + KOH \rightarrow$ ...

20. What is the volume of 47% HF having a density of 1.5 g/ml required to convert 1 g of SiO_2 into silicon tetrafluoride?

21. How many grams of magnesium silicide are needed to prepare 5.6 litres of silane gas measured at STP, and what volume of sulphuric acid having a density of 1.3 g/ml and containing 40% by mass of H_2SO_4 will be used for this preparation?

22. Silane gas, SiH_4, prepared at a temperature of electric arc from silicon and hydrogen, ignited spontaneously in air. Determine the composition and mass of the obtained products, if 8 litres of air were needed to burn silane. Write the equations for the involved reactions.

23. On burning, a mass of 12 g of silicon dioxide is obtained from a mass of 6.2 g of silicon hydride. The density of this hydride with respect to air equals 2.14 g/ml. Derive the molecular formula of the silicon hydride.

24. A precipitate is formed when ammonium sulphate is added to a solution of potassium silicate. Write down the equations for the reactions that occur here.

25. Which chemical compound can be used to identify three different solutions of potassium sulphate, potassium silicate and sodium carbonate? Write the molecular and ionic equations for the reactions that take place.

26. Which indicator can be used to identify sodium silicate, sodium sulphate, or zinc nitrate solution in three different test tubes? Write down the ionic equations for the involved reactions.

27. In the glass industry soda ash, limestone and sand are the starting materials. Describe the process of glass formation from these materials with the help of the respective equations. Sometimes soda ash is replaced in glass manufacturing by a mixture of sodium sulphate and coal. Write down the equation for the redox reaction, taking account of the fact that three gases, viz. CO, CO_2 and SO_2, are evolved.

28. The composition of glass is expressed by the formula $Na_2O \cdot CaO \cdot 6SiO_2$. Calculate the theoretical consumption of the raw materials (soda ash, limestone, and sand) to prepare 100 kg of glass.

29. Write down the formula of a silicate in the form of

a compound of oxides, if it contains 68.7% SiO_2, 19.5% Al_2O_3 and 11.8% Na_2O (all by masses).

30. Write down the formulas of the following silicates in the form of oxides: talc, $H_2Mg_3Si_4O_{12}$, albite, $Na_2Al_2Si_6O_{16}$, and anorthite, $CaAl_2Si_2O_8$.

31. What reactions are involved in the following transformations:

(a) $Si \rightarrow SiO_2 \rightarrow Na_2SiO_3 \rightarrow H_2SiO_3 \rightarrow SiO_2 \rightarrow Si$

(b) $SiO_2 \rightarrow CaSiO_3 \rightarrow CaCO_3 \rightarrow Na_2O \cdot CaO \cdot 6SiO_2$

32. Write the molecular and ionic equations for reactions with the aid of which the following transformations may be carried out:

$$\begin{array}{ccccc} SiO_2 & \rightarrow & Si & \rightarrow & Na_2SiO_3 \rightarrow H_2SiO_3 \\ \downarrow & & & & \downarrow \\ Na_2SiO_3 & \rightarrow & CaSiO_3 & \longrightarrow & SiO_2 \end{array}$$

33. Write the reaction equations to represent the following transformations:

$$\begin{array}{ccccccccc} Si & \leftarrow & SiH_4 & \longleftarrow & SiO_2 & \rightarrow & Si & \rightarrow & Na_2SiO_3 \rightarrow H_2SiO_3 \\ \downarrow & & & & & & & & \\ Mg_2Si & & & & \downarrow & & & & \downarrow \\ \downarrow & & & & & & & & \\ MgCl_2 & \rightarrow & MgSiO_3 & \rightarrow & Na_2SiO_3 & \rightarrow & CaSiO_3 & \rightarrow & SiO_2 \end{array}$$

34. Write the molecular equations for reactions expressed by the following ionic equations:

(a) $SiO_3^{2-} + 2H^+ = H_2SiO_3$

(b) $SiO_2 + 2OH^- = SiO_3^{2-} + H_2O$

(c) $H_2SiO_3 + 2OH^- = SiO_3^{2-} + 2H_2O$

35. Set up the molecular equations for reactions expressed by the following ionic equations:

(a) $Cu_2Si + 4H^+ = 2Cu^{2+} + SiH_4$

(b) $Si + 2OH^- + H_2O = SiO_3^{2-} + 2H_2$

(c) $SiH_4 + 2OH^- + H_2O = SiO_3^{2-} + 4H_2$

Write the electronic equations (half-reactions) and indicate oxidizing and reducing agents for these reactions.

36. Balance the following redox equations by the ion-electron method:

$$Si + Ba(OH)_2 + H_2O \rightarrow BaSiO_3 + H_2$$
$$SiH_4 + NaOH + H_2O \rightarrow Na_2SiO_3 + H_2$$
$$Si_2H_6 + H_2O \rightarrow SiO_2 + H_2$$

Determine the oxidant and reductant in each case.

37*. 6.1 g of sodium silicate were obtained by melting silica with soda ash. The evolved gas was absorbed by 18 ml of 10% NaOH solution having a density of 1.11 g/ml. Determine the composition of the salt formed and its mass percent in the solution.

38*. A mixture of potash and limestone was calcined with silica to yield hard glass. The liberated gas was absorbed by 270 ml of a barium hydroxide solution (also called baryta water) as a result of which 9.85 g of a precipitate were formed. Determine (a) the volume of gas absorbed by baryta water, (b) the percent strength and molar concentration of the barium hydroxide solution, if it has a density of 1.10 g/ml.

39*. A mixture of limestone and soda ash was calcined with silica for preparing ordinary glass. The liberated gas was absorbed by 17.1 g of 20% $Ba(OH)_2$ solution having a density of 1.10 g/ml until complete dissolution of the initially formed precipitate. What volume of gas was absorbed by baryta water? Determine the mass percent of the barium salt in the final solution.

40. How many tons of sand and calcium carbide (CaC_2) are needed in order to prepare 1 ton of silicon, taking into account that the other two reaction products are CaO and CO_2?

41. How many kilograms of sand containing 95% by mass of SiO_2 and how many kilograms of coal containing 98% by mass of carbon are to be taken to prepare 10 kg of carborundum, SiC?

42. How many tons of sand containing 95% by mass of SiO_2, how many tons of soda ash containing 98% by mass of Na_2CO_3, and how many tons of limestone containing 90% by mass of $CaCO_3$ are to be taken in order to prepare 1 ton of a silicate having the composition of $Na_2SiO_3 \cdot CaSiO_3 \cdot 4SiO_2$?

43. 24.4 kg of sodium silicate are prepared by fusing 20 kg of sodium hydroxide with silicon dioxide. Calculate the yield (in mass percent) of sodium silicate with respect to the theoretical amount.

44. 29 kg of calcium silicate are formed when 18 kg of sand are fused with limestone. Calculate the mass percent of silicon dioxide in the sand.

45. How many kilograms of sand, sodium carbonate, and calcium carbonate, respectively, are to be taken in order to prepare 10 kg of glass of the following composition: 73% SiO_2, 10% CaO and 17% Na_2O?

46. The composition of glass is expressed by the formula $Na_2O \cdot CaO \cdot 6SiO_2$. How many tons of sodium carbonate, calcium carbonate and silicon dioxide, respectively, are used for the preparation of 1 ton of glass?

47. Calculate the mass of silicon and the volume of 35% NaOH solution having a density of 1.38 g/ml required to prepare 33.6 litres of hydrogen at STP.

48. Calculate the mass of silicic acid which may be obtained from 40 g of sodium silicate and 73 g of hydrochloric acid containing 25% by mass of HCl.

5
METALS

5.1 GENERAL PROPERTIES OF METALS

Pure metals in solid state are crystals in which the particles are arranged in a definite geometrical order to form crystal lattices (also called space lattices). The lattice points are occupied by positively charged ions and neutral atoms, and in the space between them free electrons move.

Atoms in the crystal lattices of metals are arranged very close to one another and their valence electrons may move not only around their own atoms, but also around neighbouring atoms. Thus, the valence electrons move freely within the whole metal forming the so-called electron gas (also called "electron sea").

The presence of the free electrons in metals is confirmed by the fact that metals possess high electrical conductivity and emit free electrons on heating.

All metals, except mercury, are solid under ordinary conditions. In the compact form, that is, in the form of plates and slabs (ingots) metals possess shining, lustrous appearance. This is due to the reflection of light from their surfaces. In finely powdered state only magnesium and aluminium do retain their metallic lustre, while the powders of the other metals are either black or dark grey in colour.

Most of the metals have white-silvery colour and are nontransparent (since nearly all of them absorb long-range and short-range wavelengths of the light spectrum to the same extent). Cesium and gold are yellow, while copper is yellow-red.

In technology metals are classified as ferrous (iron, chromium, manganese and their alloys) and nonferrous (the rest of the metals). In terms of their density, light metals which have a density of less than 5 g/cm^3 (lithium, potassium, calcium, aluminium, and others) are distinguished from heavy metals with a density more than 5 g/cm^3 (tin, lead, mercury, iron and so on). Lithium (density 0.53 g/cm^3) is the lightest and osmium (density 22.5 g/m^3) is the heaviest metal. In terms of the melting point, metals are divided into low-melting, having m.p. 350°C and below (lead 327°C, tin 232°C, sodium 98°C, potassium 63°C, cesium 28°C and others) and high-melting metals exhibiting m.p. above 350°C (iron 1539°C, chromium 1875°C). Metal with the highest melting point is tungsten (m.p. 3380°C).

Two important physical properties of metals are electrical and thermal conductivity which are due to the presence of free electrons in all metals.

The best conductor of electricity is silver followed by copper, gold, chromium, aluminium, and magnesium.

Amongst the mechanical properties, malleability and ductility are characteristic of metals.

Malleability is a property of metals by virtue of which they can be hammered or pressed into new shapes (beaten into sheets) at a temperature below the melting point of the metal in question.

Ductility is the capacity of metals to be drawn into wires.

Metals with low ductility are fragile, whereas those having high ductility are strong enough to rupture. Gold

has the highest malleability and ductility. For example, 0.003-mm thick plates can be prepared and wires, nonvisible by naked eyes, can be drawn from gold. For bismuth and manganese these three qualities are in the worst position.

The common chemical property of metals is their ability only to donate electrons and to be transformed into free positively charged ions:

$$M - ne^- = M^{n+}$$

The ability to give up electrons varies from metal to metal. Whether electrons in atoms are strongly or loosely held is measured by the *ionization energy*. Alkali metals have the lowest ionization energies, and therefore they are strong reducing agents.

The reducing properties of metals account for their ability to enter into reaction with various oxidizing agents such as nonmetals, acids and salts of less active metals. The names of all compounds of metals with nonmetals end in *-ide* (e.g., oxide, chloride, nitride, sulphide, and so on). Let us consider the chemical properties of metals in detail.

1. Metals react with nonmetals.

(a) Most metals easily react with oxygen to yield oxides:

$$2Mg + O_2 = 2MgO$$

(b) They readily add halogens to afford halides:

$$2Fe + 3Cl_2 = 2FeCl_3$$

(c) Metals react with nitrogen to yield nitrides:

$$3Ba + N_2 = Ba_3N_2$$

(d) Under certain conditions metals react with sulphur to form sulphides:

$$2Al + 3S = Al_2S_3$$

It should be pointed out that the more electronegative the element, the stronger it oxidizes a metal. For example, in compounds formed by iron and chlorine, the oxidation number of iron is +3, whereas in those with sulphur, it is +2.

(e) Compounds of metals with carbon are called carbides:

$$Ca + 2C = CaC_2$$

(f) Metals react with phosphorus at 600-1200°C to afford compounds which are termed as phosphides:

$$3Li + P = Li_3P$$
$$3Zn + 2P = Zn_3P_2$$

(g) Only alkali and alkaline-earth metals can react directly with hydrogen to give hydrides:

$$2Li + H_2 = 2Li^+H^-$$
$$Ca + H_2 = Ca^{2+}H_2^-$$

(h) By reacting with silicon, metals can give silicides, for example:

$$2Mg + Si = Mg_2Si$$

According to the ability to donate electrons in solutions, metals are arranged in a series called the series of standard reduction electrode potentials or electrochemical or activity series. Hydrogen has also been placed in this series, since it is the only nonmetal which can, like metals, exist in aqueous solutions as positive ions (though in hydrated forms).

Metals are arranged in the series of standard reduction electrode potentials in order of their decreasing reducing properties in solutions or in order of the increasing oxidizing properties of their ions in solutions. Any metal given in Table 5.1 displaces the metals placed below it from their salt solutions.

Metals arranged above hydrogen replace the latter from dilute acids (except nitric acid). Alkali and alkaline-earth metals replace hydrogen even from water.

The series of standard reduction electrode potentials is valid for redox processes which take place only in aqueous media.

2. Important chemical properties of metals are reflected in their relation to water, acid solutions, alkalies, and salts.

Table 5.1 Series of Standard Reduction Electrode Potentials (or Activity Series)

Electrode			E°, V
Oxidized form	Reduced form		
Li^+	Li	↑	−3.04
K^+	K		−2.92
Ca^{2+}	Ca		−2.87
Na^+	Na		−2.71
Mg^{2+}	Mg		−2.37
Al^{3+}	Al		−1.66
Mn^{2+}	Mn		−1.18
Zn^{2+}	Zn		−0.76
Cr^{3+}	Cr		−0.74
Fe^{2+}	Fe		−0.44
Ni^{2+}	Ni		−0.25
Sn^{2+}	Sn		−0.14
Pb^{2+}	Pb		−0.13
$2H^+$	H_2		0.00
Cu^{2+}	Cu		0.34
Hg_2^{2+}	2Hg		0.79
Ag^+	Ag		0.80
Pt^{2+}	Pt		1.20
Au^{3+}	Au	↓	1.50

Increase in oxidizing properties ↓ — Increase in reducing properties ↑

Alkali and alkaline-earth metals dissolve in water to produce hydroxides (alkalies):

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2\uparrow$$

A number of heavy metals react with water on heating to yield oxides:

$$3Fe + 4H_2O \xrightarrow{t} Fe_3O_4 + 4H_2\uparrow$$

While considering the chemical reactions of metals with acids, one should take into account the acid concentration and the activity of the metal concerned (see the series of standard reduction electrode potentials).

Alkalies react only with those metals which exhibit amphoteric properties:

$$2Al + 2NaOH + 2H_2O \xrightarrow{\text{fusion}} 2NaAlO_2 + 3H_2\uparrow$$

More active metals replace the less active ones from their salt solutions:

$$Fe + CuSO_4 = FeSO_4 + Cu$$

Example 1. An iron plate with a mass of 40 g was dipped into 250 ml of $CuSO_4$ solution. Determine the mass of the deposited copper and the molar concentration of ferrous sulphate in the produced solution, if the mass of the plate after the reaction was 42 g.

Solution. Iron reacts with copper sulphate according to the equation:

$$CuSO_4 + Fe = FeSO_4 + Cu$$

for which $m\,(CuSO_4) = 160$ g, $m\,(Fe) = 56$ g, $m(FeSO_4) = 152$ g, and $m(Cu) = 64$ g. From the equation it follows that when 1 mole of copper is deposited on the iron plate, 1 mole of iron is transferred into the solution and the mass of the plate increases by $64 - 56 = 8$ g. But from the condition of the problem the mass of the plate increases by 2 g, i.e. $42 - 40 = 2$ g. So we can write

an 8-g increase is due to 64 g of deposited Cu

a 2-g increase is due to $(2 \times 64)/8 = 16$ g of deposited Cu

This means that 16 g of copper were deposited on the iron plate which correspond to $\nu = m/M = 16$ g/64 (g/mole) = 0.25 mole of copper.

It follows from the reaction equation that when 1 mole of copper is deposited on the plate, 1 mole of $FeSO_4$ is formed in the solution. Therefore, when 0.25 mole of copper is deposited, 0.25 mole of $FeSO_4$ is formed in 250 ml of solution. One litre of such a solution should contain $0.25 \times 4 = 1$ mole of $FeSO_4$ and the concentration of the solution will be 1 *M*.

Example 2. Two identical zinc plates each having a mass of 10 g were dipped into two solutions of $FeSO_4$ and $CdSO_4$. After the reactions were over, the plates were washed and dried, and were found to have masses of 9.095 g and 14.702 g, respectively. Calculate the masses of iron and cadmium which reacted in both cases. How would you account for the loss of mass for the first zinc plate and the increase in mass for the second zinc plate after the reactions?

Solution. Zinc reacts with the salt solutions according to the equations:

$$Zn + Fe^{2+} = Fe + Zn^{2+} \quad (1)$$

$$Zn + Cd^{2+} = Cd + Zn^{2+} \quad (2)$$

It follows from Eq. (1) that 1 mole of zinc replaces 1 mole of iron from the solution, that is, the change in a mass is 56—65 = —9 g. In the first solution the mass of the zinc plate decreases by 10 g — 9.095 g = 0.905 g. This means that:

a 9-g decrease is due to 56 g of deposited Fe

a 0.905-g decrease is due to $(56 \times 0.905)/9$

$= 5.6$ g of deposited Fe

In the second solution, 1 mole of zinc is transferred into the solution replacing 1 mole of cadmium, that is, the change in mass here is 112—65 = 47 g. In the second solution the mass of the plate increased by 14.702 g — 10 g = 4.702 g. So we can write:

a 47-g increase is due to 112 g of deposited Cd

a 4.702-g increase is due to $(4.702\ g \times 112\ g)/47\ g$

$= 11.2$ g of deposited Cd

Example 3. When 1.82 g of a mixture of aluminium and an unknown metal, arranged in the series of the standard reduction electrode potentials below hydrogen were dissolved in hydrochloric acid, 0.672 litre of hydrogen, measured at STP was liberated. To oxidize this mixture, 0.56 litre of oxygen measured at STP was needed. What unknown metal was taken? Determine the mass percents of the metals in the mixture.

Solution. 1. Let us first calculate the mass of aluminium in the mixture:

$$2Al + 6HCl = 2AlCl_3 + 3H_2$$

3×22.4 litres of H_2 are produced by 2×27 g of Al

0.672 litre of H_2 is produced by $\dfrac{0.672\ \text{litre} \times 2 \times 27\ g}{3 \times 22.4\ \text{litres}}$

$= 0.54$ g of Al

2. Now let us determine the volume of oxygen required to oxidize 0.54 g of Al:

$$4Al + 3O_2 = 2Al_2O_3$$

4×27 g of Al need 3×22.4 litres of O_2

0.54 g of Al needs $0.54 \text{ g} \times 3 \times 22.4 \text{ litres}/(4 \times 27) \text{ g} = 0.336$ litre of O_2

3. The volume of oxygen required to oxidize the unknown metal equals $0.56 - 0.336 = 0.224$ litre and its mass is $1.82 \text{ g} - 0.54 \text{ g} = 1.28$ g.

4. Now we can calculate the atomic mass of the unknown metal:

0.224 litre of O_2 oxidizes 1.28 g of metal

22.4 litres of O_2 oxidize $\dfrac{1.28 \text{ g} \times 22.4 \text{ litres}}{0.224 \text{ litre}} = 128$ g of metal

But none of the monovalent metals in the activity series below hydrogen has the atomic mass of 128 amu. So the given unknown metal is divalent with an atomic mass of 128/2 = 64 amu. This atomic mass is for copper.

5. At last, let us determine the mass percent of aluminium in the mixture:

1.82 g of mixture constitute 100%

0.54 g of Al constitutes $(0.54 \text{ g} \times 100\%)/1.82 \text{ g} = 29.67 \approx 30\%$

Therefore, the unknown metal is copper and the mixture contains 30% of Al and 100—30 = 70% of Cu.

Example 4. A mass of 6.3 g of a mixture of metals, sodium and calcium, was dissolved in water to liberate 3.36 litres of a gas measured at STP. How many grams of each metal were there in the mixture?

Solution. Method 1. The metals react with water according to equations:

$$2Na + 2H_2O = 2NaOH + H_2$$
$$Ca + 2H_2O = Ca(OH)_2 + H_2$$

Let us assume that the whole mixture consists of sodium alone. In this case, the volume of liberated hydrogen may be calculated as follows:

46 g of Na evolve 22.4 litres of H_2

6.3 g of Na evolve 6.3 g $\times$ 22.4 litres/46 g

$= 3.06$ litres of H_2

Likewise, assuming the whole mixture to be made up of calcium alone, we can determine the volume of liberated hydrogen:

40 g of Ca liberate 22.4 litres of H_2

6.3 g of Ca liberate 6.3 g $\times$ 22.4 litres/40 g

$= 3.53$ litres of H_2

In the first case we have a deficit of hydrogen (3.36 litres — 3.06 litres = 0.3 litre), while in the second case we have an excess of it (3.53 litres — 3.36 litres = 0.17 litre). The ratio of deficit to excess is 0.3 : 0.17 = 1.7 : 1. The sum of these two fractions is 1.7 + 1 = 2.7. Therefore, the given mixture contains $(6.3 \times 1)/2.7 = 2.3$ g of sodium, and $(6.3 \times 1.7)/2.7 = 4$ g of calcium.

Method 2. Let X be the mass of sodium (in g) in the mixture. Then the mass of calcium will be $(6.3 - X)$ g. Now let us determine the volume of hydrogen liberated as a result of reaction with X g of Na:

46 g of Na liberate 22.4 litres of H_2

X g of Na will liberate $22.4\ X/46$ litres of H_2

Likewise, we can determine the volume of hydrogen liberated when $(6.3 - X)$ g of Ca react with water:

40 g of Ca give 22.4 litres of H_2

$(6.3 - X)$ g of Ca give $22.4 \times (6.3 - X)/40$ litres of H_2

So, we can write now

$$\frac{22.4X}{46} + \frac{22.4\,(6.3 - X)}{40} = 3.36, \text{ whence } X = 2.3$$

This means that the given mixture contains 2.3 g of Na and 6.3 — 2.3 = 4 g of Ca.

PROBLEMS AND EXERCISES

1. Which position in the periodic table do metals occupy?
2. What is the difference between the outermost energy levels of metals and nonmetals?
3. What is the malleability of metals due to?
4. How do metals differ from nonmetals in physical properties?
5. Which features of the internal structure of metals underlie their thermal and electrical conductivity?
6. Which of the periods and Groups in the Mendeleev's periodic table consist completely of metals?
7. On the basis of electron distribution in energy level of atoms indicate which of the following elements should be brought under metals: 2, 8; 2, 8, 18, 18, 4; 2, 8, 9, 2; 2, 8, 18, 32, 14, 2; 2, 8, 18, 6; 2, 8, 3. Justify your answer.
8. Which metals can react with alkalies?
9. How are hydroxides of active metals prepared?
10. What is aluminothermy?
11. Which metals can displace hydrogen from hydrochloric and dilute sulphuric acids?
12. What is called the series of standard reduction electrode potentials (or the electrochemical or activity series)?
13. In which case alloys are called solid solutions?
14. How do the properties of pure metals differ from those of alloys?
15. Which metals form soluble hydroxides by reacting with water?
16. Name two metals in each case: (a) nonferrous, (b) ferrous, (c) the lightest and the heaviest, (d) the highest-melting, (e) the best conductors of heat and electricity, (f) the most malleable.
17. State whether the mass of aluminium will increase or not on reacting with solutions of (a) $Mg(NO_3)$, and (b) $Pb(NO_3)_2$.
18. Write the molecular and ionic equations for the possible reactions between (a) cobalt and dilute nitric acid, (b) iron and magnesium sulphate, (c) nickel(II) sulphate and zinc, (d) calcium and water, (e) aluminium

and potassium hydroxide, (f) concentrated sulphuric acid and mercury.

19. With which solutions will iron react: HNO_3, H_2SO_4, H_2CO_3, $MgSO_4$, $CuCl_2$, KOH? Write the molecular and ionic equations to represent the possible reactions.

20. An aluminium plate was dipped into a mixture of lead(II) nitrate and copper(II) sulphate solutions. Write the molecular and ionic equations for the involved reactions.

21. Complete the following redox reactions:

(a) $Zn+HNO_3 \rightarrow NH_4NO_3+\ldots$

(b) $Sr+H_2SO_4 \rightarrow H_2S+\ldots$

(c) $Al+NaOH \rightarrow H_2+\ldots$

(d) $K+H_2O \rightarrow H_2+\ldots$

22. Write the equations for reactions between water and (a) lithium, (b) magnesium, (c) aluminium, (d) iron, and (e) barium.

23. Write the equations for reactions between iron and (a) HCl, (b) concentrated, hot, and dilute H_2SO_4, respectively, (c) concentrated, hot, and dilute HNO_3, respectively, and (d) H_2S.

24. Write the equations for reactions between zinc and (a) KOH, (b) conc. HNO_3, (c) dil. H_2SO_4, and (d) H_2O.

25. Write the ionic equations for the possible reactions between (a) zinc and silver nitrate, (b) cupric nitrate and nickel, (c) aluminium chloride and silver, and (d) mercuric sulphate and iron.

26. Write the ionic equations for the possible reactions between (a) zinc and barium hydroxide, (b) magnesium and sodium hydroxide, (c) aluminium and potassium hydroxide, and (d) chromium and sodium hydroxide.

27. What will happen with an iron plate having a mass of 5 g, if it is held in a solution containing 1.6 g of copper sulphate?

28. When 6 g of a mixture of aluminium and copper were treated with hydrochloric acid, 3.7 litres of hydrogen measured at STP were collected. Determine the mass percents of the metals in the mixture.

29. How many grams of magnesium oxide are obtained by burning 12 g of magnesium?

30. When copper reacted with concentrated sulphuric acid, 33.6 litres of a gas measured at STP were formed. Determine the mass of copper which entered into the reaction.

31. A mass of 10 g of a mixture of iron and copper powders was treated with a hydrochloric acid solution. As a result, 2.24 litres of a gas measured at STP evolved. Determine the mass percents of the metals in the mixture.

32. How many millilitres of 40% NaOH solution (density 1.43 g/ml) will be needed to dissolve 9 g of aluminium?

33. A volume of 3.808 litres of hydrogen measured at STP was evolved when 4 g of an alloy of zinc with aluminium were dissolved in an alkali. Determine the mass percents of the metals in the alloy.

34. A drop of a salt solution of an unknown metal was placed on a copper plate. After some time the plate was washed with distilled water. In the place where there was the solution drop, a lustrous spot remained which disappeared on heating. Which metal constitutes the salt? Explain the formation of the shining spot and write down the corresponding reactions.

35. A mass of 3 g of technical-grade iron was treated with 0.2 *M* hydrochloric acid solution to liberate 1.12 litres of a gas measured at STP. Determine the mass percent of pure iron in the technical-grade metal. What volume of acid is consumed to dissolve pure iron?

36. Dissolution of 8.6 g of a mixture of potassium and potassium oxide in 30 ml of water yielded 1.12 litres of a gas measured at STP. Determine the percent strength of the solution thus obtained.

37. Sulphuric acid having a density of 1.814 g/ml and containing 90% by mass of H_2SO_4 was used to dissolve 4 g of a mixture of copper and cupric oxide. The volume of a liberated gas was 1.12 litres (STP). What volume of acid was used to dissolve the mixture?

38. When copper was heated with concentrated sulphuric acid containing 96 mass % H_2SO_4, a gas was evolved which was used to neutralize 500 ml of a potassium hydroxide solution having a density of 1.14 g/ml and containing 15% by mass of KOH. How many grams of copper and sulphuric acid, respectively, were employed?

39*. A mass of 1.76 g of a mixture of iron and copper was treated with 7 ml of hot 70% H_2SO_4 solution having a density of 1.6 g/ml. Determine the composition of the mixture. How much and which gas was evolved as a result of the reaction?

40*. A mixture of copper and iron containing 60% by mass of iron was treated (without heating) with a sulphuric acid solution having a density of 1.14 g/ml and containing 60% by mass of H_2SO_4. Determine the mass of this mixture, if 112 ml of a gas were evolved as a result of the reaction, and the volume of the sulphuric acid solution that entered into the reaction.

41*. A mass of 54 g of silver was obtained by dissolving a mixture of iron and copper filings in a silver nitrate solution. When the same quantity of the same metal mixture was put into a blue vitriol solution, the mass of the filings increased by 0.8 g. Determine the mass percents of the metals in the mixture. How many millilitres of a nitric acid solution having a density of 1.40 g/ml and containing 65% by mass of HNO_3 may enter into reaction with the copper filings of the mixture?

42*. When 0.5 g of a mixture of magnesium, aluminium, and copper was treated with a sodium hydroxide solution, 336 ml of a gas were evolved. By treating the same amount of the mixture with hydrochloric acid, 448 ml of a gas were obtained. (Gas volumes were measured at STP.) Determine the mass percents of the three metals in the mixture. What volume of 14% NaOH solution having a density of 1.145 g/ml will be required to treat 10 g of the metal mixture?

43*. When a mixture of iron, copper and aluminium was oxidized on heating with an excess oxygen, 5.32 litres of the latter entered into reaction. The same mixture reacted with 120 ml of 5 *M* hydrochloric acid solution. When the same amount of the metal mixture was treated with a sodium hydroxide solution, 1.12 litres of hydrogen measured at STP evolved. Determine the mass percents of iron, copper, and aluminium in the mixture.

44*. 13.3 g of NaOH were needed for a reaction with a definite mass of a mixture of copper, iron, and aluminium. Chlorination of the same amount of metal mixture required 12.5 litres of chlorine measured at STP, while 23.2

litres of hydrochloric acid were used for a reaction to proceed with the same quantity of the metal mixture. Determine the mass percents of the metals in the mixture.

45*. When 32.6 g of a mixture of tin and lead were treated with hot dilute hydrochloric acid, 4.48 litres of a gas measured at STP evolved, while when dilute sulphuric acid was used, the volume of a gas measured at STP was 2.24 litres. Determine the mass percents of the components in the mixture.

46*. Recovery of tin from tin food cans (with subsequent electrolysis of sodium stannate) is carried out according to the equation:

$$Sn+2NaOH+O_2=Na_2SnO_3+H_2O$$

What volume of 40% NaOH solution having a density of 1.2 g/ml will be required to dissolve the whole tin contained in 1000 such cans, if each of them has 0.4 g of tin?

5.2 GROUP IA OR ALKALI METALS

Alkali metals occupy Group IA in Mendeleev's periodic table. These are lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr).

Atoms of the alkali metals contain one electron in the outermost quantum layer (or shell). Their penultimate quantum layers have the stable electronic configuration of noble gases, s^2p^6 (for lithium, s^2).

These elements are soft metals. They have low melting points (varying between 180 and 30°C) which decrease regularly throughout the Group from lithium to cesium.

Because of their strong chemical activity, the alkali metals occur in nature only in the form of compounds. Compounds of sodium and potassium are the most abundant, while those of the remaining alkali metals occur in nature very rarely.

Chemical properties of the alkali metals are similar. The metals form compounds mainly with ionic bonds, since they readily give up the *s* electron from the outermost shell. These metals are readily oxidized in air. To prevent oxidation, they are stored in closed vessels under

kerosene. On heating they react with air to produce peroxides (with the exception of lithium which forms Li_2O).

The vapours of alkali metals impart characteristic colours to the flame, e.g. red for Li, yellow for Na, violet for K, violet-rose for Rb and blue for Cs. The alkali metals react readily with halogens and sulphur. They yield hydrides when heated with hydrogen.

In the electrochemical series all these metals are arranged above hydrogen. They are easily oxidized by water to give hydroxides. These metals replace hydrogen from water according to the equation:

$$2M^0 + 2HOH = H_2\uparrow + 2MOH$$

When these metals are heated at 350-400°C in an atmosphere of hydrogen, they afford hydrides:

$$2Na + H_2 = 2NaH \qquad 2K + H_2 = 2KH$$

In the hydrides hydrogen is electronegative.

The hydroxides of the alkali metals are hygroscopic, readily absorb CO_2 from air, and destroy glass. They dissociate in aqueous solutions almost completely.

The alkali metals replace hydrogen from those acids which are not oxidizing agents, e.g. HCl, dil. H_2SO_4:

$$2HCl + 2M = 2MCl + H_2\uparrow$$

$$H_2SO_4\ (dil.) + 2M = M_2SO_4 + H_2\uparrow$$

While reacting with oxidizing acids such as conc. H_2SO_4, conc. and dil. HNO_3, these metals do not replace hydrogen; H_2S, N_2O and NH_3 are, respectively, formed instead:

$$5H_2SO_4\ (conc.) + 8M = 4M_2SO_4 + H_2S + 4H_2O$$

$$10HNO_3\ (conc.) + 8M = 8MNO_3 + N_2O + 5H_2O$$

$$9HNO_3\ (dil.) + 8M = 8MNO_3 + NH_3 + 3H_2O$$

Most alkali metal salts are colourless and soluble in water.

Example 1. A mass of 22 g of sodium hydroxide was added to a solution containing 19.6 g of phosphoric acid. The final solution was evaporated to dryness. Determine which salts and in what amounts were formed.

Solution. Phosphoric acid reacts with sodium hydroxide according to the equations

$$\underset{98}{H_3PO_4} + \underset{40}{NaOH} = \underset{120}{NaH_2PO_4} + H_2O$$

$$NaH_2PO_4 + NaOH = \underset{142}{Na_2HPO_4} + H_2O$$

$$Na_2HPO_4 + NaOH = \underset{164}{Na_3PO_4} + H_2O$$

It is given that 19.6 g or 19.6/98 = 0.2 mole of phosphoric acid react with 22 g or 22/40 = 0.55 mole of sodium hydroxide. The molar ratio between phosphoric acid and sodium hydroxide equals 0.2 : 0.55 = 1 : 2.75. From the reaction equations it is evident that when the molar ratio is 1 : 1, only monosubstituted phosphate is formed, while for the molar ratios of 1 : 2 and 1 : 3 the respective salts are disubstituted and trisubstituted phosphates. Now if the ratio is less than 1 : 1 a mixture of phosphoric acid and monosubstituted phosphate is formed, if the ratio is less than 1 : 2 the product is a mixture of mono- and disubstituted salts, whereas when the ratio is less than 1 : 3, the product is a mixture of di- and trisubstituted sodium phosphates.

In the given case the molar ratio of phosphoric acid and sodium hydroxide is 1 : 2.75 which is less than 1 : 3. This means that in this case a mixture of di- and trisubstituted sodium phosphates is formed. 0.2 mole of phosphoric acid reacts with 0.4 mole of sodium hydroxide to yield 0.2 mole of the disubstituted phosphate. The remaining 0.15 mole (0.55—0.4 = 0.15) of sodium hydroxide will react with 0.15 mole of the disubstituted phosphate to produce 0.15 mole of the trisubstituted salt. In this way, 0.2 mole of phosphoric acid reacts with 0.55 mole of sodium hydroxide to produce 0.15 mole of sodium phosphate (a trisubstituted salt) and 0.05 mole (0.2 — 0.15 = = 0.05) of disodium hydrogen phosphate (a disubstituted salt).

Example 2. A volume of 56 ml of CO_2 (STP) is produced when 1 g of a mixture of sodium carbonate and bicarbonate is calcined. The residue thus obtained is treated with an excess hydrochloric acid to evolve 168 ml of CO_2 measured at STP. Calculate the mass percents of the initial salts in the mixture.

Solution. It follows from the equation for decomposition of sodium bicarbonate

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

that 2 moles of $NaHCO_3$ produce 1 mole each of CO_2 and Na_2CO_3. Therefore, we can write

1 mole of CO_2 is formed from 2×84 g of $NaHCO_3$

0.0025 mole of CO_2 is formed from $(2 \times 84$ g $\times 0.0025$ mole$)/1$ mole $= 0.42$ g of $NaHCO_3$

Here 56 ml of CO_2 at STP equal 0.0025 mole of CO_2. Now we determine the mass of Na_2CO_3:

2×84 g of $NaHCO_3$ yield 106 g of Na_2CO_3

0.42 g of $NaHCO_3$ yields $0.42 \text{ g} \times 106 \text{ g}/(2 \times 84)$ g $= 0.265$ g of Na_2CO_3

During treatment with the acid, carbon dioxide is liberated both from 0.265 g of Na_2CO_3 formed by decomposition of $NaHCO_3$, and from Na_2CO_3 contained in the initial mixture:

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$$

Let A be the mass of Na_2CO_3 in the initial mixture. Then we can say that $(A + 0.265)$ g of Na_2CO_3 yielded 168 ml of CO_2. Now

106 g of Na_2CO_3 liberate 22400 ml of CO_2

$(A + 0.265)$ g of Na_2CO_3 liberate $(A + 0.265) \times 22400/106$ ml of CO_2

Therefore

$(A + 0.265) \times 22400/106 = 168$, whence

$A = 0.53$ g of Na_2CO_3

In this way, the initial mixture having a mass of 1 g contained 0.42 g of $NaHCO_3$ (42%), 0.53 g of Na_2CO_3 (53%) and $1 - (0.42 + 0.53) = 0.05$ g of impurities (5%).

Example 3. 64 g of a mixture of NaCl and KCl were treated with concentrated sulphuric acid. The total mass of

sulphates obtained was found to be 76 g. What are the mass percents of NaCl and KCl in the mixture?

Solution. Let X be the mass of NaCl and Y be the mass of KCl in the mixture. Then $X + Y = 64$ g. The given chlorides react with concentrated sulphuric acid as follows:

$$2NaCl(s)+H_2SO_4\ (conc.) \xrightarrow{t} Na_2SO_4+2HCl\uparrow$$
$$2KCl(s)+H_2SO_4\ (conc.) = K_2SO_4+2HCl\uparrow$$

We can write from the first chemical equation

2×58 g of NaCl produce 142 g of Na_2SO_4

X g of NaCl produces $X \times 142/(2 \times 58)$

$= 1.214X$ g of Na_2SO_4

Likewise, it follows from the second chemical equation that

2×74.5 g of KCl produce 174 g of K_2SO_4

Y g of KCl produces $Y \times 174/(2 \times 74.5)$

$= 1.167Y$ g of K_2SO_4

So the second algebraic equation is $1.214X + 1.167Y = 76$. Solving the two algebraic equations we get

$$X = 24 \text{ g and } Y = 40 \text{ g}$$

Therefore, the mass percents of KCl and NaCl in the mixture are $24 \times 100/64 = 37.5\%$ NaCl and $40 \times 100/64 = 62.5\%$ KCl.

PROBLEMS AND EXERCISES

1. Why are the Group IA elements called alkali metals?
2. Why are the alkali metals stored in closed vessels under kerosene?
3. Which colours do sodium and potassium salts impart to the flame?
4. Which alkali metal is the lightest one? How does hardness change in the vertical row containing alkali metals?
5. Which sodium and potassium compounds are the most widespread in nature?

6. Is it possible to prepare a solution of sodium or potassium (a) in water? (b) in kerosene? How can water be detected in kerosene, if one of the alkali metals is available?

7. Metallic potassium ignites spontaneously in a chlorine atmosphere, whereas in air it is oxidized rather slowly. Why?

8. How can alkali metals be prepared?

9. Which compounds are formed on burning alkali metals in air?

10. Why should alkali metal hydroxides be stored in tightly closed containers?

11. Which salts are obtained by reacting sodium hydroxide with (a) carbon dioxide, (b) sulphur trioxide, and (c) hydrogen choride?

12. How will you prepare the following sodium compounds: (a) peroxide, (b) hydride, (c) hydroxide, and (d) bicarbonate?

13. How can the following substances be prepared from potassium hydroxide: (a) metallic potassium, (b) oxygen, (c) potassium sulphide, and (d) potassium carbonate?

14. How will you convert sodium chloride into (a) nitrate, (b) sulphate, and (c) hydroxide?

15. What is the chemical composition of the following compounds: (a) soda water, (b) caustic soda, and (c) crystalline soda?

16. Which of the following salts are hydrolyzed: KNO_3, $KHCO_3$, K_2SiO_3, and Na_2S? State whether the aqueous solution of each of these salts is acidic, basic or neutral.

17. Write down the equations for reactions involved in the following transformations:

(a) $Na \rightarrow Na_2O_2 \rightarrow Na_2O \rightarrow NaOH \rightarrow NaCl$

(b) $NaNO_3 \rightarrow NaHSO_4 \rightarrow Na_2SO_4 \rightarrow NaCl \rightarrow Na$

18. Write down the equations to represent reactions that take place when the following conversions are carried out:

(a) $K \rightarrow KOH \rightarrow KHCO_3 \rightarrow K_2CO_3$

(b) $KOH \rightarrow K_2ZnO_2 \rightarrow Zn(OH)_2 \rightarrow Zn(HS)_2$

19. With which of the following compounds will sodium hydroxide react: hydrochloric acid, magnesium oxide,

carbon dioxide, zinc hydroxide, and calcium hydroxide? Write the equations for the involved reactions.

20. 3.9 g of potassium were dissolved in 206.2 ml of water. Determine the percent strength of the solution thus produced.

21. A substance contains 17.9% carbon, 47.77% oxygen, and 34.33% sodium (by mass). Its molecular mass equals 134. Derive the true formula of the substance.

22. How many grams of potassium did react with water if 4.48 litres of a gas measured at STP were evolved? How many grams of potassium hydroxide were formed as a result of this reaction?

23. 0.86 g of a metal replaces 246.4 ml of a gas (STP) from water. What metal is this?

24. Which redox processes take place, when alkali metals react with water, when alkalies react with aluminium and with silicon? Write down the electronic equations (half-reactions) for these processes.

25. Which salts can be prepared by reacting sodium hydroxide with (a) chlorine, (b) sulphur dioxide, and (c) hydrogen sulphide? Write the equations for the reactions that occur.

26. Which of the following salts are hydrolyzed: KCl, Na_2CO_3, K_2S, and Na_2SO_4? Write the molecular and ionic equations for the hydrolysis reactions.

27. How many litres of oxygen can be prepared by the action of 10 g of carbon dioxide on sodium peroxide?

28. A compound consists of sodium, silicon and oxygen whose masses are in the ratio of $m(Na) : m(Si) : m(O) = 23 : 14 : 24$. Determine the formula of the compound.

29. Chlorine was passed through a hot KOH solution. How much KOH will be required for reacting with 1.2 litres of chlorine measured at STP, if one of the reaction products is $KClO_3$?

30. After the removal of water of crystallization from 2.5 g of crystal hydrate of soda its mass reduced to 0.926 g. Calculate the mass percent of water in the crystal hydrate and deduce its formula.

31*. 5.06 g of a mixture of sodium hydroxide and sodium carbonate were neutralized with 500 ml of 0.3 *M* sulphuric acid solution. Determine the mass percents of

NaOH and Na_2CO_3 in the mixture and the volume of carbon dioxide evolved during neutralization.

32. A volume of 100 ml of hydrochloric acid having a density of 1.1 g/ml and containing 20% by mass of HCl was used to neutralize a certain amount of a sodium hydroxide solution. How many millilitres of 10% H_2SO_4 solution (density 1.07 g/ml) will be needed to neutralize the same amount of the sodium hydroxide solution?

33*. Determine the concentration of a sodium hydroxide solution which is obtained by mixing 40 g of 15% NaOH solution with 16.4 ml of 20% NaOH solution (density 1.22 g/ml). How many litres of carbon dioxide can be absorbed by the final sodium hydroxide solution, if a neutral salt is formed? Determine the mass percent of this salt in the solution after the absorption of carbon dioxide.

34*. 6.85 g of a mixture of sodium bicarbonate and soda were neutralized with 25 ml of 2 *M* sulphuric acid solution. The liberated gas was absorbed by lime water, and 7.5 g of a precipitate were produced. Determine the mass percents of the components in the mixture and the volume of the liberated gas.

35*. When 6.08 g of a mixture of Glauber's salt and crystalline soda (sodium carbonate decahydrate) were calcined, the mass of the evolved water was 3.6 g. Determine the mass percents of the components in the mixture. How many millilitres of 30% H_2SO_4 solution (density 1.22 g/ml) are to be used to convert the whole of soda, contained in the mixture, into sodium sulphate?

36. During calcination of 5.24 g of a mixture of calcium carbonate and bicarbonate, 1.344 litres of carbon dioxide evolved. Determine the mass percents of the components in the mixture. What volume of 20% NaOH solution (density 1.25 g/ml) should be taken to completely absorb the liberated carbon dioxide?

37. Calculate the masses of sodium hydroxide and sodium carbonate in 2.92 g of a mixture of these two compounds, if 1 litre of 0.06 *M* hydrochloric acid solution is required to form sodium chloride from this mixture.

38. Calculate the mass percents of potassium bicarbonate and potassium hydroxide in 25.6 g of the initial mixture, if after calcination and cooling the loss of mass was 4.9 g.

39. Calculate the masses of $Na_2CO_3 \cdot 10H_2O$ and water required to prepare 500 g of a solution which is supposed to contain 10.6% by mass of Na_2CO_3.

40. Calculate the mass percent of potassium chloride in a natural mineral called sylvinite, KCl·NaCl.

41. What mass of sodium is to be dissolved in water in order to produce the same volume of hydrogen as that obtained by dissolving 78 g of potassium in water?

42. Carbon dioxide, obtained by decomposing 200 g of calcium carbonate, was passed through a solution containing 60 g of sodium hydroxide. Determine the mass of the salt formed in the solution. Name the salt.

43. Calculate the masses of potassium nitrate and sodium nitrate in 14.56 g of their mixture, if 12 g of potassium nitrite and sodium nitrite were formed after calcination of the above mixture.

44. Calculate the masses of sodium and potassium chlorides in 1.74 g of their mixture, if 3.77 g of a precipitate are formed when an excess silver nitrate is added.

5.3 GROUP IIA METALS

The elements beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra), constitute Group IIA of the periodic table.

The atoms of the elements of Group IIA have two electrons in their outermost shell. The penultimate layer has, as in the case of the alkali metals, 8 electrons (s^2p^6), the only exception being beryllium which contains 2 electrons in the penultimate layer, that is, in the *s* sublevel. The reducing power of the Group IIA elements is weaker than that of the alkali metals.

These are soft metals; their hardness varies from 1.5 to 4 in the Mohs hardness scale. All, except for Ba, belong to light metals. The boiling and melting points of these metals change irregularly. This irregularity is accounted for by different structures of their crystal lattices.

The Group IIA metals do not occur in nature in free state. Calcium, which is a constituent part of a large number of compounds, is the most abundant element in

Group IIA. Each of these elements has a lot of natural isotopes. Unlike the rest of the Group IIA elements, radium is a radioactive element.

Ca, Sr, Ba, and Ra are termed as alkaline-earth metals, for their oxides ("earths" as alchemists used to call them) form alkalies with water. Beryllium and magnesium differ in their properties from the alkaline-earth metals. Beryllium resembles Al, while Mg resembles Zn.

The chemical properties of alkaline-earth metals are determined by the ease with which they can give up two electrons from the outermost shell under the action of oxidants:

$$M - 2e^- = M^{2+}$$

The metals of Group IIA (except for Be) are unstable in air and covered by oxide films. Calcium, strontium, and barium are stored in air-tight containers.

On heating, the alkaline-earth metals react vigorously with hydrogen, halogens, oxygen, sulphur, nitrogen, phosphorus, carbon, and silicon.

Calcium, strontium, and barium decompose water at ordinary temperatures to liberate hydrogen and to yield hydroxides, whereas beryllium and magnesium, only at elevated temperatures. The general equation is

$$M + 2H_2O = M(OH)_2 + H_2\uparrow$$

In terms of chemical properties, the alkaline-earth metal hydroxides are weaker than the alkali metal hydroxides. The former are sparingly soluble in water and their basic nature increases throughout Group IIA. For example, $Be(OH)_2$ is amphoteric in nature, $Mg(OH)_2$, $Ca(OH)_2$, and $Ba(OH)_2$ are, respectively, weak, strong, and very strong bases.

With acid solutions all of them react to yield the respective salts. Most salts of alkaline-earth metals (Ca, Sr, Br) such as fluorides, sulphates and phosphates are sparingly soluble in water.

Example 1. During decomposition of 14.2 g of a mixture of calcium carbonate and magnesium carbonate 3.36 litres of carbon dioxide (STP) are evolved. Determine the mass percents of the carbonates in the mixture.

Solution. Decomposition of calcium carbonate and magnesium carbonate takes place according to the equations

$$CaCO_3 \xrightarrow{t} CaO + CO_2 \qquad MgCO_3 \xrightarrow{t} MgO + CO_2$$

It follows from the given equations that 1 mole of calcium carbonate with $M_r = 100$ or magnesium carbonate with $M_r = 84$ produces 1 mole of CO_2. In the given case 3.36 litres or 3.36 litres/22.4 litres·mole^{-1} = 0.15 mole of carbon dioxide were evolved. The given mixture contained, therefore, a total of 0.15 mole of calcium and magnesium carbonates. Let X be the number of moles of calcium carbonate and $(0.15 - X)$ be the number of moles of magnesium carbonate in the mixture. Then the mixture contains $100X$ g of calcium carbonate and $84(0.15 - X)$ g of magnesium carbonate. So we can write

$$100X + 84 \times (0.15 - X) = 14.2, \text{ whence } X = 0.1$$

Thus the mixture contains

$$m(CaCO_3) = M(CaCO_3)\,\nu = 100 \text{ g/mole} \times 0.1 \text{ mole} = 10 \text{ g}$$

$$m(MgCO_3) = M(MgCO_3)\,\nu = 84 \text{ g/mole} \times 0.05 \text{ mole} = 4.2 \text{ g}$$

Therefore, the mass percents of the salts in the mixture are

$$\frac{10 \times 100}{14.2} = 70.4\%\ CaCO_3, \qquad \frac{4.2 \times 100}{14.2} = 29.6\%\ MgCO_3$$

Example 2. After calcining 4.42 g of a mixture of marble and malachite, 2.72 g of a nonvolatile residue remained. Determine the masses of the carbonates in the mixture. How can calcium be isolated in a pure state from the original mixture?

Solution. 1. The equations for the reactions that take place during calcination are

$$CaCO_3 = CaO + CO_2 \qquad (CuOH)_2CO_3 = 2CuO + H_2O + CO_2$$

for whith $m(CaCO_3) = 100$ g, $m(CaO) = 56$ g, $m[(CuOH)_2CO_3] = 222$ g, and $m(CuO) = 2 \times 80$ g $=$ $= 160$ g. Now we obtain a set of algebraic equations with two unknowns, in which X is the mass (in g) of marble and Y is that of malachite:

$$X + Y = 4.42 \text{ and } \frac{56X}{100} + \frac{160Y}{222} = 2.72$$

Solving, $X = 2.9$ and $Y = 1.52$, that is, the given mixture consists of 2.9 g of marble and 1.52 g of malachite.

2. In order to get calcium in pure state, the mixture should first be treated with hydrochloric acid. The involved reactions may be represented by the following equations:

$$CaCO_3+2HCl = CaCl_2+H_2O+CO_2$$
$$(CuOH)_2CO_3+4HCl = 2CuCl_2+3H_2O+CO_2$$

In the electrolysis of the obtained solution copper is deposited at the cathode. The following reactions take place at the electrodes:

$$CuCl_2 \rightleftharpoons Cu^{2+}+2Cl^-$$
$$H_2O \rightleftharpoons H^++OH^-$$

at cathode: $Cu^{2+}+2e^- = Cu$

at anode: $2Cl^- - 2e^- = Cl_2$

Now the solution contains calcium chloride only. The solution is evaporated to dryness to get solid calcium chloride which is then electrolyzed in the molten state to yield pure calcium. The involved reactions are:

$$CaCl_2 \rightleftharpoons Ca^{2+}+2Cl^-$$

at cathode: $Ca^{2+}+2e^- = Ca$

at anode: $2Cl^- - 2e^- = Cl_2$

Example 3. A mass of 0.3 g of a mixture of zinc oxide and magnesium oxide was dissolved in 17 ml of 1 *M* hydrochloric acid. The excess acid was then neutralized with 8 ml of 0.5 *M* sodium hydroxide solution. Calculate the mass percents of the oxides in the mixture.

Solution. Method 1. The given oxides react with HCl according to the following equations:

$$MgO+2HCl = MgCl_2+H_2O$$
$$ZnO+2HCl = ZnCl_2+H_2O$$

Now 8 ml of 0.5 *M* NaOH solution contain $0.008 \times \times 0.5 = 0.004$ mole of NaOH, while 17 ml of 1 *M* hydrochloric acid contain $0.017 \times 1 = 0.017$ mole of HCl, of which 0.004 mole of HCl, which constitutes the excess amount, is neutralized by alkali and $0.017 - 0.004 = = 0.013$ mole is used to dissolve the given mixture of zinc and magnesium oxides.

Let X be the mass of MgO (in g) and Y be the mass of ZnO (in g).
Then we can write

$$X + Y = 0.3$$

40 g of MgO react with 2×36.5 g of HCl

X g of MgO reacts with $73X/40$ g of HCl

And, 81 g of ZnO react with 73 g of HCl

Y g of ZnO reacts with $73Y/81$ g of HCl

Thus we can have a second algebraic equation

$$\frac{73X}{40} + \frac{73Y}{81} = \frac{13 \times 36.5}{1000} = 0.4745$$

Solving these algebraic equations we get

$$Y = 0.079 \text{ g of ZnO (26.3\%)}$$

$$X = 0.3 - 0.079 = 0.221 \text{ g of MgO (73.7\%)}$$

Method 2. 0.013 mole of HCl is 0.4745 g of HCl. Now assuming that the whole mixture consists of ZnO alone, we can determine the amount of acid used:

81 g of ZnO react with 73 g of HCl

0.3 g of ZnO reacts with $(0.3 \times 73)/81 = 0.2703$ g of HCl

But if the whole mixture is assumed to be made of MgO alone, we get:

40 g of MgO react with 73 g of HCl

0.3 g of MgO reacts with $(0.3 \times 73)/40 = 0.5475$ g of HCl

In the case of ZnO, the deficit of acid is $0.4745 - 0.2703 = 0.2042$ g and in the case involving MgO, the acid excess is $0.5475 - 0.4745 = 0.073$ g. The ratio of deficit to excess is $0.2042 : 0.073 = 2.8 : 1$. So the total number of parts equals $2.8 + 1 = 3.8$. Thus the mixture consists of

$$\text{MgO} = \frac{0.3 \times 2.8}{3.8} = 0.221 \text{ g}$$

$$\text{ZnO} = \frac{0.3 \times 1}{3.8} = 0.079 \text{ g}$$

Example 4. Titration of 0.2 litre of water containing calcium bicarbonate required 0.08 litre of hydrochloric

acid with $c(HCl) = 0.001$ mole/litre. Determine the temporary hardness of water.

Solution. Hardness of water is determined by the molar concentration of an equivalent of Ca^{2+} and Mg^{2+} ions in millimoles per litre of water. While dealing with these types of problems, it is necessary to take into account that the volumes of reacting solutions are inversely proportional to their concentrations, i.e.,

$$V_1 : V_2 = c_2 : c_1, \text{ or } V_1c_1 = V_2c_2$$

where V_1 and V_2 are the volumes of solutions consumed in the reaction, and c_1 and c_2 are their concentrations. Using this relationship, we can calculate the molar concentration of an equivalent of Ca^{2+} ions present in the given calcium bicarbonate:

$$c_2 = \frac{V_1c_1}{V_2} = \frac{0.08 \text{ litre} \times 0.001 \text{ mole/litre}}{0.2 \text{ litre}} = 0.0004 \text{ mole/litre}$$

which corresponds to 0.4 mmole/litre or 0.4 milliequivalent/litre. Hardness of water in the given case is, therefore, 0.4 milliequivalent/litre.

Example 5. Determine the total hardness of 4 litres of water which contains 220 mg of $Ca(HCO_3)_2$ and 160 mg of $Mg(HCO_3)_2$.

Solution. Method 1. Hardness of water is expressed in milliequivalents of Ca^{2+} and Mg^{2+} ions (or their relevant salts) per litre of water as follows:

$$H_{H_2O} = \frac{m_1}{Eq_1V} + \frac{m_2}{Eq_2V}$$

where m_1 and m_2 are the masses of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$, respectively, Eq_1 and Eq_2 are the equivalents of these two salts, and V is the volume of water. Now the values of Eq_1 and Eq_2 are

$$Eq_1 = M\left[\frac{1}{2}\,Ca(HCO_3)_2\right] = \frac{162.11}{2} = 81.05$$

$$Eq_2 = M\left[\frac{1}{2}\,Mg(HCO_3)_2\right] = \frac{146.34}{2} = 73.17$$

Therefore,

$$H_{H_2O} = \frac{220}{81.05 \times 4} + \frac{160}{73.17 \times 4} = 0.642 + 0.553$$

$$= 1.195 \text{ milliequivalents/litre}$$

Method 2. Amount of $Ca(HCO_3)_2$ in 1 litre of hard water:

4 litres contain 220 mg of $Ca(HCO_3)_2$

1 litre contains (1 litre $\times$ 220 mg)/4 litres

$= 55$ mg of $Ca(HCO_3)_2$

Amount of $Mg(HCO_3)_2$ in 1 litre of hard water:

4 litres contain 160 mg of $Mg(HCO_3)_2$

1 litre contains (1 litre $\times$ 160 mg)/4 litres

$= 40$ mg of $Mg(HCO_3)_2$

Concentration of Ca^{2+} ions in 1 litre of H_2O:

162 mg of $Ca(HCO_3)_2$ contain 40 mg of Ca^{2+}

55 mg of $Ca(HCO_3)_2$ contain (55 mg $\times$ 40 mg)/162 mg

$\doteq 13.57$ mg of Ca^{2+}

Concentration of Mg^{2+} ions in 1 litre of H_2O:

146 mg of $Mg(HCO_3)_2$ contain 24 mg of Mg^{2+}

40 mg of $Mg(HCO_3)_2$ contain (40 mg $\times$ 24 mg)/146 mg

$= 6.57$ mg of Mg^{2+}

Hence, the hardness of water equals

$$H_{H_2O} = \frac{m(Ca^{2+})}{M\left(\frac{1}{2}Ca^{2+}\right)} + \frac{m(Mg^{2+})}{M\left(\frac{1}{2}Mg^{2+}\right)} = \frac{13.58}{20.04} + \frac{6.57}{12.16}$$

$= 1.217$ milliequivalents/litre

PROBLEMS AND EXERCISES

1. Why are the elements of calcium subgroup called alkaline-earth metals?
2. What are the similarities and what are the differences in the properties of alkaline-earth and alkali metals?
3. How is calcium oxide prepared?
4. What are the reactions that take place when alkaline-earth metals react with water?
5. How will you distinguish between slaked lime and finely ground limestone?
6. Which alkaline-earth metals are radioactive?

7. Carbon dioxide is passed through lime water. At first, a precipitate is formed which then dissolves as CO_2 passing is continued. How would you explain this?
8. What chemical reactions accompany lime hardening?
9. How do the properties of the alkaline-earth metal hydroxides change down the Group?
10. What is the chemical composition of gypsum, chalk, slaked lime, nonslaked lime, bleaching powder, and limestone?
11. Which chemical reaction underlies the use of plaster of Paris?
12. Why does marble dissolve in sulphuric acid slowly and incompletely?
13. Water containing magnesium chloride should not be used for steam boilers. Why?
14. Which salts impart hardness to water?
15. Name the methods by which hardness of water can be removed.
16. Which units are used to express hardness? How water is classified in terms of hardness?
17. Which hardness of water is called (a) total, (b) temporary, (c) permanent, (d) carbonate, (e) noncarbonate?
18. What is "baryta water"? Why does it become turbid in air?
19. Why is $BaCO_3$ soluble in weak acids, whereas $BaSO_4$ is sparingly soluble even in strong ones?
20. Why do $CaCO_3$ and $MgCO_3$ dissolve in natural water?
21. With which of the following solutions will metallic calcium react: HNO_3, KOH, $FeSO_4$, HBr? Write the equations for the involved reactions.
22. Write down the molecular and ionic equations for the reactions between calcium and (a) water, (b) conc. HNO_3, (c) conc. H_2SO_4, (d) HCl.
23. How can the following compounds be identified if water and nitric acid are available: chalk, gypsum, soda, apatite? Explain your answer and give the respective reaction equations.
24. Carbon dioxide had been passed through lime water until a transparent liquid was formed. The solution was

then evaporated off. What is the solid residue thus obtained? Write down the equations for the involved reactions.

25. Complete the following reactions with balanced equations:

$$Ca + ? \rightarrow H_2 + \ldots; \qquad CaC_2 + ? \rightarrow C_2H_2 + \ldots$$
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3; \qquad CaCO_3 + ? \rightarrow Ca^{2+} + \ldots$$

26. Can the following pairs of ions exist simultaneously in solutions: (a) Ca^{2+} and $H_2PO_4^-$, (b) Ca^{2+} and HCO_3^-, (c) Ca^{2+} and CO_3^-, (d) Ca^{2+} and NO_3^- and (e) Ca^{2+} and PO_4^{3-}?

27. Complete the following equations for reactions representing them in molecular and ionic forms:

(a) $Ca(OH)_2 + CO_2 = \ldots$ (b) $CaCO_3 + H_2O + CO_2 = \ldots$

(c) $CaCO_3 + HCl = \ldots$ (d) $Ca(OH)_2 + NaHCO_3 = \ldots$

(e) $Ca(HCO_3)_2 + Ca(OH)_2 = \ldots$ (f) $CaO + CH_3COOH = \ldots$

28. Write the equations for reactions involved in the following conversions:

$$Ca \rightarrow Ca(OH)_2 \rightarrow \text{calcium hydroxosulphate} \rightarrow CaSO_4$$
$$\rightarrow Ca(OH)_2 \rightarrow \text{calcium aluminate}$$

29. Write the reaction equations to represent the following transformations:

$$Ca \rightarrow Ca(OH)_2 \rightarrow CaCO_3 \rightarrow Ca(HCO_3)_2$$

30. Write the equations for reactions used to carry out the following conversions:

$$CaCl_2 \rightarrow Ca(NO_3)_2 \rightarrow Ca_3(PO_4)_2 \rightarrow Ca(H_2PO_4)_2$$

31. Determine the mass percents of calcium in the following naturally occurring compounds: $CaCO_3$, $CaSO_4 \times \times 2H_2O$, $Ca_3(PO_4)_2$.

32. How many litres of carbon dioxide may be obtained from 25 g of limestone which contains 20% by mass of impurities?

33. How many kilograms of calcium oxide are formed when 250 kg of limestone are calcined which contain 80% by mass of calcium carbonate?

34. How many grams of calcium oxide and water, respectively, are required in order to prepare 0.5 mole of slaked lime?

35. How much calcium bicarbonate will react with slaked lime to yield 250 g of calcium carbonate?

36. How many grams of calcium hydroxide are to be added to 162 g of a calcium bicarbonate solution containing 5% by mass of $Ca(HCO_3)_2$ to yield the relevant neutral (or normal) salt?

37. Which of the following compounds can be used to remove carbonate (or temporary) hardness of water caused by the presence of calcium bicarbonate: Na_2CO_3, $Ca(OH)_2$, NaCl, HCl? Justify your answer using the respective equations for the involved reactions.

38. Which of the following compounds are used to remove noncarbonate (or permanent) hardness of water caused by the presence of calcium sulphate: NaOH, Na_2CO_3, NaCl, Na_2S? Explain your answer with the aid of the relevant equations.

39. Determine the total hardness of water, 500 ml of which contain 30 and 24 mg of $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$, respectively.

40. Write down the equations for the reactions which will take place when soda is added to hard water containing $Mg(HCO_3)_2$, $CaCl_2$, $MgSO_4$ and $Ca(HCO_3)_2$.

41. The hardness of water equals 4.35 milliequivalents per litre. How much soda should be added to 1 m^3 of this water in order to convert it into soft water?

42*. When 39 g of a mixture of calcium carbonate and unslaked lime were treated with an acetic acid solution, 5.6 litres of a gas measured at STP were evolved. Determine the mass percents of the components in the mixture and the volume of 8.8 *M* acetic acid solution which entered into the reaction.

43*. What is the mass percent of barium hydroxide in a solution obtained by dissolving 9.18 g of barium oxide in 300 ml of water? How many millilitres of 0.5 *M* sulphuric acid solution are to be added to neutralize the barium hydroxide solution?

44. A mass of 1.73 g of a mixture of calcium and strontium carbonates was roasted. At a temperature above 1000°C 1.07 g of a mixture of new solid products were formed. Calculate the masses of the carbonates in the mixture.

45. Roasting of 248 g of a mixture of calcium and stron-

tium carbonates yielded 160 g of a mixture of solid oxides. Calculate the molar ratio of the carbonates in the original mixture.

46. How much calcium carbonate is formed when 0.8 litre of carbon dioxide is passed through lime water?

47. Calculate the mass percents of calcium hydroxide and calcium carbonate in a mixture, if the mass of the residue after roasting constituted 60% of the initial mass.

48. A volume of 448 ml of a gas (STP) was liberated when 2 g of a mixture of calcium metal and calcium oxide were treated with water. How much calcium hydroxide is formed when 10 g of the same mixture are treated with water?

49. What is the maximum volume of carbon dioxide at STP which may be absorbed by a solution containing 200 g of calcium hydroxide?

50. Determine the mass percents of calcium in the, following naturally occurring compounds: $CaSO_4 \cdot 2H_2O$ $Ca_3(PO_4)_2$ and $CaCO_3$.

51. What mass of calcium bicarbonate should react with slaked lime to yield 350 g of $CaCO_3$?

52. 5 ml of 0.1 *M* hydrochloric acid solution were used for reaction with calcium bicarbonate, contained in 100 ml of water. Calculate the carbonate hardness of this water.

53. On mild heating gypsum ($CaSO_4 \cdot 2H_2O$) liberates 75% of the water of crystallization to yield plaster of Paris. Derive the formula of the plaster of Paris.

54. Calculate the masses of calcium and magnesium carbonates in 24.6 g of their mixture, if 0.27 mole of CO_2 was consumed for the formation of this mixture.

55. How many grams of calcium bicarbonate were present in a solution, if 10 ml of a 5% solution of an acid (density 1.024 g/ml) were used for the reaction?

5.4 GROUP IIIA ELEMENTS

Group IIIA of the periodic table consists of boron (B), aluminium (Al), gallium (Ga), indium (In), and thallium (Tl). All these elements, except for boron, are metals.

The outermost shell of these elements contains three electrons: two in the *s* and one in the *p* sublevel. The charac-

teristic oxidation number for all of them is +3. Thallium can exhibit an oxidation number of +1.

The structure of the penultimate quantum shell in the atoms of these elements is different. The penultimate shells of B and Al have noble gas configurations, whereas Ga, In, and Tl have 18 electrons each in the penultimate shell.

The metallic properties in Group IIIA elements are less pronounced as compared to those in the Group IA and IIA elements, since the elements of Group IIIA donate electrons with difficulty.

The Group IIIA metals are silvery-white and comparatively soft (hardness in the Mohs' scale varies from 1.1 to 2.6). They have relatively low melting points. Gallium has the lowest melting point of 29.8°C.

These metals are chemically active. They react with halogens and sulphur to yield compounds with an oxidation number of +3.

They react with water in different ways. Al reacts with water on heating:

$$2Al+6H_2O=2Al(OH)_3+3H_2$$

while in the absence of oxygen even boiling water does not react with Ga and In. Metallic Tl reacts with water in the presence of air to yield a strong hydroxide, TlOH and to evolve hydrogen. Like alkali metals, thallium is stored in air-tight containers under kerosene, glycerine or vaseline oil.

Al, Ga, and In react with dilute mineral acids such as HCl, H_2SO_4. Tl does not react with these acids due to the formation of a sparingly soluble film of TlCl or Tl_2SO_4 (salt passivation).

Concentrated HNO_3 and H_2SO_4 passivate aluminium at low temperatures forming an oxide film which is insoluble in acids. Aluminium dissolves in hot sulphuric acid:

$$2Al+6H_2SO_4\ (conc.) \xrightleftharpoons{t} Al_2(SO_4)_3+3SO_2\uparrow+6H_2O$$

Aluminium readily dissolves in alkalies:

$$2Al+2KOH+2H_2O \xrightleftharpoons{fusion} 3H_2\uparrow+2KAlO_2$$

$$2Al+2KOH+6H_2O=2K[Al(OH)_4]+3H_2$$

Aluminium easily removes oxygen from the oxides of other metals. During the reaction of aluminium with metal oxides, a large amount of heat is evolved:

$$Cr_2O_3+2Al=2Cr+Al_2O_3+Q$$

$$3Mn_3O_4+8Al=9Mn+4Al_2O_3+Q$$

The reduction of metal oxides by aluminium is called *aluminothermy*. This process is used for the preparation of metals that are reduced with difficulty and have high-melting points (titanium, tungsten, molybdenum, zirconium, vanadium and others). Aluminium oxide and hydroxide exhibit amphoteric properties, that is, dissolve both in acids and alkalies.

Example 1. A mass of 2.72 g of an alloy containing lead, aluminium, and copper was dissolved in nitric acid containing 50% by mass of HNO_3. When a sulphuric acid solution was added, 1.515 g of a precipitate A appeared. Hydrogen sulphide gas was then passed into the remaining solution. A second precipitate was formed which when calcined in air produced 1.6 g of a compound B. Determine the composition of the alloy.

Solution. All the three metals present in the given alloy dissolve in the given 50% nitric acid solution to afford a mixture of nitrates. When sulphuric acid is added to these nitrates, $PbSO_4$ precipitate (compound A) is formed

$$Pb(NO_3)_2+H_2SO_4=2HNO_3+PbSO_4\downarrow$$

1. Let us calculate the amount, in grams, of lead present in 1.515 g of compound A:

303 g of $PbSO_4$ contain 207 g of Pb

1.515 g of $PbSO_4$ contain $1.515\times 207/303=1.035$ g of Pb

2. On passing H_2S, CuS precipitates, while Al_2S_3 does not precipitate due to its hydrolysis:

$$Cu(NO_3)_2+H_2S=CuS\downarrow+2HNO_3$$

When calcined, the precipitate CuS forms cupric oxide (CuO) according to the equation:

$$2CuS+3O_2=2CuO+2SO_2$$

Let us now calculate the mass of copper present in 1.6 g of compound B (CuO):

80 g of CuO have 64 g of Cu

1.6 g of CuO have $1.6 \times 64/80 = 1.28$ g of Cu

3. The mass of aluminium equals

$$m(\text{Al}) = 2.72 - (1.035 + 1.28) = 0.405 \text{ g}$$

Thus, the given alloy consists of 0.405 g of Al, 1.28 g of Cu and 1.035 g of Pb.

Example 2. To carry out reaction with an alkali, a mixture of copper, iron and aluminium required 13.33 g of NaOH. During chlorination the same amount of metal mixture entered into reaction with 12.5 litres of chlorine measured at STP, while for treating the same amount of metal mixture 343.64 ml of hydrochloric acid, having a density of 1.1 g/ml and containing 10% by mass of HCl, were required. Determine the mass percents of the metals in the mixture.

Solution. 1. Of the three metals in the given mixture only aluminium does react with alkali. So let us calculate how many grams of aluminium there are in the mixture:

$$2\text{Al} + 2\text{NaOH} + 10\text{H}_2\text{O} = 2\text{Na}[\text{Al(OH)}_4(\text{H}_2\text{O})_2] + 3\text{H}_2$$

2×40 g of NaOH consume 2×27 g of Al

13.33 g of NaOH consume $2 \times 27 \times 13.33/(2 \times 40)$

≈ 9 g of Al

2. How many grams of hydrochloric acid are needed for reaction with 9 g of Al to take place?

$$2\text{Al} + 6\text{HCl} = 2\text{AlCl}_3 + 3\text{H}_2$$

2×27 g of Al need 6×36.5 g of HCl

9 g of Al need $9 \times 6 \times 36.5/(2 \times 27)$

$= 36.5$ g of HCl

3. Now let us calculate the mass, m, of HCl present in 343.64 ml of 10% HCl solution whose density is 1.1 g/ml:

$$\%) = (m/m_1)\,100\% = 100\,m\,(V\rho)\%, \text{ since } m_1 = V\rho$$

Therefore

$$m = \frac{cV\rho}{100} = \frac{10 \times 343.64 \times 1.1}{100} = 37.8 \text{ g}$$

This means that 37.8 — 36.5 = 1.3 g of HCl will react with Fe.

4. How many grams of Fe are there in the mixture?

$$Fe + 2HCl = FeCl_2 + H_2$$

2×36.5 g of HCl need 56 g of Fe

1.3 g of HCl need $1.3 \times 56/(2 \times 36.5)$

$= 0.997$ g of Fe

5. How many litres of chlorine did enter into a reaction with 0.997 g of Fe?

$$2Fe + 3Cl_2 = 2FeCl_3$$

2×56 g of Fe consume 3×22.4 litres of Cl_2

0.997 g of Fe consumes 0.997×3

$\times 22.4$ litres/(2×56) g $= 0.598$ litre of Cl_2

6. How many litres of chlorine did enter into a reaction with 9 g of Al?

$$2Al + 3Cl_2 = 2AlCl_3$$

2×27 g of Al take up 3×22.4 litres of Cl_2

9 g of Al take up 9 g $\times 3 \times 22.4$ litres/(2×27) g

$= 11.2$ litres of Cl_2

7. Fe and Al together react with 0.598 + 11.2 = 11.798 litres of chlorine. Therefore, (12.5 — 11.798) = 0.7 litre of chlorine is to react with copper.

8. The mass of copper present in the given mixture may now be calculated as follows:

$$Cu + Cl_2 = CuCl_2$$

22.4 litres of Cl_2 react with 64 g of Cu

0.7 litre of Cl_2 reacts with 0.7 litre $\times$ 64 g/22.4 litres

$= 2$ g of Cu

9. The total mass of the mixture is 9 g of Al + 0.997 g of Fe + 2 g of Cu. This constitutes about 12 g.

10. Hence the mass percents of Fe, Cu and Al in the given mixture are 8.3% Fe, 75% Al and 16.7% Cu.

PROBLEMS AND EXERCISES

1. In terms of abundance in nature, what place amongst the other elements does aluminium occupy?
2. In the form of which compounds does aluminium occur in nature? Does aluminium occur in nature in a free state?
3. After storing in air, a film of aluminium oxide and hydroxide was formed on the surface of an aluminium plate. How will you remove this film by chemical means without causing any harm to the metal?
4. What is the method of preparation of metallic aluminium?
5. How many electrons are there in the ion Al^{3+}? The electronic configuration of which "noble gas" is similar to that of the ion Al^{3+}?
6. What is aluminothermy?
7. State in brief the general characteristics of the hydroxides of the metals of aluminium subgroup.
8. What will be the colours of the indicators, litmus and phenolphthalein, in aqueous solutions of (a) $Al(NO_3)_3$, (b) $NaAlO_2$ and (c) $KAl(SO_4)_2$?
9. What is obtained when (a) aluminium, (b) aluminium oxide and (c) aluminium hydroxide are treated with concentrated sodium hydroxide solution?
10. Which of the following hot solutions containing 10% by mass of the respective solutes should not be stored in aluminium vessels: (a) sodium carbonate, (b) sulphuric acid, (c) zinc sulphate, (d) nitric acid?
11. Which type of salt does alum belong to? Where is it used in industry?
12. Which mineral of aluminium forms the basis of the following precious stones: sapphire, ruby and emerald? Impurities of which metals impart these stones different colours?
13. Explain why aluminium sulphide is not precipitated when solutions of aluminium nitrate and sodium sulphide are mixed together. Determine the composition of the precipitate thus formed.

14. What is a thermite mixture?

15. When $KAl(SO_4)_2$ is treated with a solution of Na_2S or Na_2CO_3 a precipitate of similar composition is formed. Why?

16. Write the equations for the reactions of aluminium with dilute and concentrated (a) sulphuric, (b) hydrochloric and (c) phosphoric acids.

17. Write the molecular and ionic equations for the reactions of (a) aluminium, (b) aluminium oxide and (c) aluminium hydroxide with concentrated potassium hydroxide solution.

18. How many kilograms of aluminium are needed in order to prepare 10 kg of chromium from chromium oxide by the aluminothermic process?

19. When 9 g of aluminium are burnt, 17 g of aluminium oxide are formed. Determine the equivalent of aluminium.

20*. How much metallic aluminium may enter into a reaction with the substance left in a solution after electrolysis of 100 ml of 5.85% NaCl solution (density 1.00 g/ml)?

21. The thermochemical equation for the combustion reaction of a thermite mixture is as follows:

$$8Al+3Fe_3O_4=9Fe+4Al_2O_3+2610\ kJ$$

What amount of heat will be liberated when 108 g of aluminium is burnt?

22. Write the thermochemical equation for the combustion reaction of 28 g of aluminium in oxygen to liberate 860 kJ of heat.

23. Write down the equations for the reactions given below:

(a) $Al_2O_3+? \rightarrow [Al(OH)_4(H_2O)_2]^-+?$

(b) $Al+? \rightarrow Al^{3+}+?$

(c) $Al(OH)_3+? \rightarrow AlO_2^-+?$

(d) $Al^{3+}+? \rightarrow Al+?$

24. Write down the equations for the hydrolysis of $Al_2(SO_4)_3$, $AlCl_3$, $Al(CH_3COO)_3$ and Al_2S_3.

25. Deduce the formula of a compound, whose molecular mass is 318 and which contains 17 mass % aluminium, 22.6 mass % carbon and 60.4 mass % oxygen.

26. When 6 g of an alloy of copper and aluminium were treated with potassium hydroxide, 4.704 litres of a gas measured at STP were evolved. Determine the mass percents of the components in the alloy.

27. How many millilitres of 40% NaOH solution having a densiy of 1.43 g/ml are required in order to dissolve 14.1 g of a mixture of aluminium and aluminium oxide, if this is accompanied by the liberation of 11.2 litres of a gas at STP?

28. When 20 g of a mixture of aluminium and copper were treated with concentrated nitric acid, 4.48 litres of a gas at STP were evolved. Determine the mass percents of the metals in the mixture.

29. Use the ion-electron method for balancing the following redox reactions:

$$AlCl_3+NaNO_2+H_2O \rightarrow Al(OH)_3+NaCl+NO+NO_2$$

$$Al_2O_3+C+N_2 \rightarrow AlN+CO$$

$$Al+Ag_2S \rightarrow Al_2S_3+Ag$$

30. To 100 ml of 0.28 *M* NaOH solution (density 1.11 g/ml) were added 200 ml of another NaOH solution which has a density of 2.21 g/ml and contains 19 mass percent of NaOH. Determine the mass percent of NaOH in the final solution. What volume will occupy (at STP) the gas liberated when aluminium reacts with this (final) solution?

31. When a mixture of aluminium and magnesium was treated with a sodium hydroxide solution, 11.2 litres of hydrogen measured at STP were liberated, while when the same amount of this mixture was treated with hydrochloric acid, 33.6 litres of hydrogen, also measured at STP, were evolved. Determine the composition of the mixture.

32*. When a mass of 1.82 g of a mixture of aluminium and an unknown metal, lying in the activity series below hydrogen, was dissolved in hydrochloric acid, a volume of 0.672 litre of hydrogen was evolved. To oxidize this mixture, a volume of 0.56 litre of oxygen, measured at STP, was needed. What metal other than Al was taken? Determine its mass percent in the mixture.

33. How much sodium hydroxide solution with a density of 1.33 g/ml and 30 mass % NaOH was required in

order to dissolve the whole of aluminium in a mixture containing copper as the second component, if this gave off a volume of 3.36 litres of a gas, measured at STP? Determine the mass of the mixture which entered into the above reaction, given that the mixture contains 25 mass% aluminium.

34*. A mass of 2.22 g of a mixture of iron and aluminium turnings when dissolved in hydrochloric acid which has a density of 1.09 g/ml and contains 18.25% by mass of HCl liberated a volume of 1344 ml of hydrogen, measured at STP. Find out the mass percent of each metal in the mixture and determine how many millilitres of the hydrochloric acid were required to dissolve a mass of 2.22 g of the metal mixture.

35*. A mixture consists of two metals with oxidation numbers of +3 and +2, respectively. When a mass of 11.75 g of this mixture was treated with an excess alkali solution, a volume of 6.72 litres of a gas was evolved. The residue having a mass of 6.35 g was dissolved in concentrated sulphuric acid to give off a volume of 2.24 litres of SO_2. Which metals constitute the mixture?

36. How much aluminium is required to obtain hydrogen needed to reduce cupric oxide which is obtained by decomposing a mass of 6.66 g of malachite, $(CuOH)_2CO_3$?

37*. To the salt, prepared by reacting a mass of 30 g of aluminium with a mass of 48 g of sulphur, was added an excess water. The liberated gas was passed through a volume of 10 litres of 0.2 *M* cadmium sulphate solution. Write down the equations for the reactions that take place above and calculate the final concentration of cadmium sulphate in mole per litre. It is assumed that the liberated gas all enters into the reaction.

38. The gas evolved at the anode during the industrial preparation of aluminium was passed through a volume of 1.456 litres of a potassium hydroxide solution, which has a density of 1.1 g/ml and contains 10.5% by mass of KOH, until complete absorption. Determine the mass percent of the salt formed and the mass of aluminium deposited at the cathode.

39. Calculate the masses of copper and aluminium in a mass of 3 g of their mixture, if a mass of 10 g of a sodium hydroxide solution containing 24 mass % NaOH was re-

quired to absorb the gas liberated when the mixture was treated with an excess concentrated nitric acid.

40. Calculate the mass of aluminium which when dissolved in hydrochloric acid or an alkali liberates a volume of 6.72 litres of a gas at STP.

41. Determine what should be the mass ratio of the samples of aluminium and magnesium which when dissolved in a nitric acid solution would give equal volumes of nitrogen.

42. Calculate the volume of hydrogen formed when a mass of 81 g of aluminium is treated with an excess alkali.

43. A mixture of aluminium and copper was treated with an alkali solution. The liberated gas when burnt in air yielded a mass of 27 g of water. Calculate the mass of aluminium in the metal mixture.

44. Calculate the mass of aluminium required to prepare a mass of 112 g of iron from magnetite, Fe_3O_4.

45. What volume of hydrogen will be liberated if 27 g of aluminium react with 140 ml of a sodium hydroxide solution containing 20 % by mass of NaOH?

46. 2.2 kg of aluminium oxide are required for smelting 2 kg of aluminium from it. Calculate the yield (in %) of aluminium relative to the theoretical amount.

47. 50 g of a mixture of aluminium and iron were treated with 40% NaOH solution having a density of 1.43 g/ml. This resulted in the liberation of a volume of 11.2 litres of a gas measured at STP. Determine the mass percents of the metals in the mixture and the volume of the alkali required for the reaction.

48. Calculate the mass percent of impurities in a technical-grade aluminium, if 10.6 litres of a gas measured at STP were liberated when a 9-g sample of it was treated with an excess sodium hydroxide solution.

49. Calculate the mass of a sodium hydroxide solution containing 6% by mass of NaOH required for a reaction with 10 ml of an aluminium chloride solution which has a density of 1.04 g/ml and contains 5% by mass of $AlCl_3$ to produce the aluminate, $NaAlO_2$.

50. How much aluminium chloride is required in order to prepare 0.5 litre of 0.2 *M* solution?

5.5 GROUP VIB METALS

The metals, chromium (Cr), molybdenum (Mo), and tungsten (W) constitute Group VIB. These are also referred to as the metals of chromium subgroup. The *d* sublevels of the penultimate shells of the atoms of these elements are incomplete.

All these metals form compounds with an oxidation number of +6 due to the electrons in the outermost shell and *d* electrons in the penultimate shell. Besides, molybdenum and tungsten can form stable compounds with an oxidation number of +4, while chromium forms stable compounds in which it can have oxidation numbers of +2 and +3.

All the three elements are similar in chemical properties and are extremely stable at ordinary temperatures. At elevated temperatures, however, they react with halogens, oxygen, sulphur, nitrogen, phosphorus, carbon, silicon and boron. These metals form alloys with a number of other metals, mainly with heavy ones.

But since the atomic radii of these metals are different, there are certain differences in chemistry of these elements. The values of radii are close for molybdenum and tungsten, but differ from that of chromium. Unlike chromium, molybdenum and tungsten do not form divalent compounds. Numerous stable complexes of trivalent chromium differ in their properties from complexes involving Mo or W. In physical properties chromium also differs from the other two metals.

As far as occurrence in nature is concerned, Mo and W belong to rare and scattered elements, while chromium is abundant in nature.

Example 1. How does chromium react with dilute and concentrated acids and with alkalies?

Solution. Under ordinary conditions, chromium is stable to a number of chemical reagents. This is why it is widely used as protective coating. Chromium reacts slowly with hydrochloric or dilute sulphuric acid after the oxide film has been dissolved:

$$Cr + 2HCl = CrCl_2 + H_2$$

$$Cr + H_2SO_4 = CrSO_4 + H_2$$

This metal does not dissolve in cold nitric or concentrated sulphuric acids, nor does it dissolve in aqua regia, since the oxide film is strengthened in these acids. It dissolves, however, in hot concentrated sulphuric acid to give off SO_2:

$$2Cr+6H_2SO_4\ (conc.)=Cr_2(SO_4)_3+3SO_2+6H_2O$$

At high temperatures chromium reacts with molten alkalies:

$$2Cr+3KOH+2H_2O=2KCrO_2+3H_2$$

Example 2. Oxygen, potassium chromate and chromic oxide are obtained by decomposing $K_2Cr_2O_7$. The liberated oxygen all reacted with 20.4 g of chromium. Chromium trioxide was obtained when potassium chromate had been treated with concentrated sulphuric acid. How much chromic oxide and how much chromium trioxide were obtained, assuming that the volume of oxygen had been measured at STP?

Solution. The reactions that take place above may be represented as follows:

$$4K_2Cr_2O_7=2Cr_2O_3+4K_2CrO_4+3O_2 \quad (1)$$

$$4Cr+3O_2=2Cr_2O_3 \quad (2)$$

$$K_2CrO_4+H_2SO_4=CrO_3+K_2SO_4+H_2O \quad (3)$$

Let us calculate the volume of oxygen consumed on the basis of Eq. (2):

4×51 g of Cr consume 3×22.4 litres of O_2

20.4 g of Cr consume $20.4\ g\times 3$

$\times 22.4$ litres/(4×51) g = 6.72 litres of O_2

Likewise, we can calculate the mass of isolated chromic oxide from the same Eq. (2):

4×51 g of Cr yield 2×150 g of Cr_2O_3

20.4 g of Cr yield $20.4\ g\times 2\times 150$ g/(4×51) g

$=30$ g of Cr_2O_3

From Eq. (1) we can determine the masses of the liberated Cr_2O_3 and K_2CrO_4:

3×22.4 litres of O_2 correspond to 2×150 g of Cr_2O_3

6.72 litres of O_2 correspond to 2×150 g $\times 6.72$ litres/(3×22.4) litres $= 30$ g of Cr_2O_3

Thus a total of $30 + 30 = 60$ g of Cr_2O_3 was obtained.

3×22.4 litres of O_2 correspond to 4×193 g of K_2CrO_4

$$6.72 \text{ litres of } O_2 \text{ correspond to } \frac{6.72 \text{ litres} \times 4 \times 193 \text{ g}}{3 \times 22.4 \text{ litres}} = 77.2 \text{ g of } K_2CrO_4$$

Finally, from Eq. (3) we get the mass of CrO_3:

193 g of K_2CrO_4 produce 99 g of CrO_3

77.2 g of K_2CrO_4 produce (77.2 g $\times$ 99 g)/193 g $= 39.6$ g of CrO_3

Therefore, 60 g of Cr_2O_3 and 39.6 g of Cr_2O_3 were obtained as a result of the whole process.

PROBLEMS AND EXERCISES

1. What is the position of chromium in Mendeleev's periodic table?
2. How do the elements of Groups VIA and VIB differ in electronic structures and properties?
3. What oxidation numbers are typical of chromium?
4. Determine the oxidation numbers of chromium in the following compounds: $Cr_2(SO_4)_3$, $K_2Cr_2O_7$, $BaCrO_4$ and $(BiO)_2Cr_2O_7$.
5. What properties do the compounds of trivalent and hexavalent chromium exhibit in redox reactions?
6. $KCr(SO_4)_2$ yields a precipitate of the same composition when treated with either Na_2S solution or K_2CO_3 solution. Why?
7. Which metal should be used to replace chromium from $CrCl_3$: Mg, Sn, Cu, Hg?
8. Which of the following substances react with each other: (a) $Cr(OH)_3$ and KOH; (b) Cr_2O_3 and SiO_2; (c) $Cr(NO_3)_3$ and $MgCl_2$; (d) K_2CrO_4 and H_2SO_4; (e) $Na_2Cr_2O_7$ and NaOH; (f) Cr_2O_3 and H_2O?

9. In which of the following solutions will Cr_2O_3 dissolve: $Ba(OH)_2$, H_2SO_4, KNO_3?

10. Name the following compounds of chromium: K_2CrO_4, $H_2Cr_2O_7$, $CrSO_4$, $NaCrO_2$ and K_3CrO_3. What are the valences of chromium in these compounds?

11. What reagents are to be added to chromic hydroxide in order to prepare (a) sodium chromite, (b) chromic sulphate?

12. What products are obtained when (a) potassium dichromate and (b) aluminium dichromate are heated in air?

13. Chromium forms an oxide with oxygen that contains 23.5% oxygen and 76.5% chromium (by mass). Determine the equivalent of chromium and write down the formula of the oxide.

14. Write down the reaction equations which permit to determine the chemical nature of the oxides Cr_2O_3 and CrO_3. What volume of 40% NaOH solution which has a density of 1.42 g/ml is needed to dissolve 25.2 g of a mixture of these oxides containing 60.3% by mass of chromic oxide?

15. 20 g of $Cr(NO_3)_3$ were added to 400 g of 10% $Cr(NO_3)_3$ solution. Determine the molarity of the final solution, if its density equals 1.15 g/ml.

16. Write down the graphic formulas for the following compounds: $Cr_2(SO_4)_3$, $K_2Cr_2O_7$, $NaCr(SO_4)_2$ and $CrOH(NO_3)_2$. Write the equations for dissociation of these compounds.

17. What products are obtained by mixing a solution of sodium carbonate with that of chromic chloride or a solution of potassium sulphide with that of chromic sulphate? Write the equations for the respective reactions with a view to the hydrolysis of the produced salts.

18. How much chromic oxide and nitrogen (in volume units) are produced when 27 g of ammonium dichromate are decomposed? The dichromate contains 7.41 mass percent of impurities.

19. CrO_3 may be obtained by treating barium chromate with an excess concentrated nitric acid. Write down the equation for this reaction and determine the mass of CrO_3 produced from 12.6 g of barium chromate.

20. How will you prepare chromium from sodium

dichromate? Write the equations for the involved reactions.

21. 114 kg of chromic oxide were reduced with aluminium. Determine the mass of aluminium required to reduce the oxide and the mass of the produced chromium.

22. Derive the formula of a compound which contains 17.56% sodium, 39.7% chromium and 42.74% oxygen (by mass).

23. Write the electrochemical equations for the electrolysis of $Cr_2(SO_4)_3$ and $CrCl_3$ solutions in the following cases: (a) the anode is made up of carbon and (b) the anode is made up of chromium.

24. Write the molecular equation for the hydrolysis of a salt expressed below by an ionic equation:

$$Cr^{3+}+HOH \rightleftharpoons (CrOH)^{2+}+H^+$$

25. Write down the molecular and ionic equations for the reactions that take place between (a) $Cr(OH)_3$ and HCl, (b) $Cr(OH)_3$ and KOH, (c) $K_2Cr_2O_7$ and KOH and (d) K_2CrO_4 and H_2SO_4.

26. Cite examples of reactions shown schematically below:

(a) $Cr_2O_3+? \rightarrow CrO_2^-+H_2O$

(b) $Cr(OH)_3+? \rightarrow Cr(OH)_6^{3-}$

(c) $Cr+? \rightarrow Cr^{3+}+?$

27. Write the following chemical equations in the ionic form:

(a) $2KCrO_2+3Br_2+8KOH=6KBr+2K_2CrO_4+4H_2O$

(b) $Cr_2(SO_4)_3+3H_2O_2+10NaOH=3Na_2SO_4+2Na_2CrO_4+8H_2O$

(c) $K_2Cr_2O_7+14HI=2KI+2CrI_3+3I_2+7H_2O$

28. Write down the molecular and ionic equations for the reactions which would exhibit that Cr_2O_3 is amphoteric and CrO_3 is acidic in nature.

29. An excess sodium hydroxide solution was added to a solution of chromic chloride. To the liquid thus obtained was added bromine water. What compounds are formed as a result of such mixing? Write down the equations for the involved reactions.

30. For the following redox reactions write down the equations to represent the half-reactions and balance

them:

$$Cr(OH)_3+H_2O_2+NaOH \rightarrow Na_2CrO_4+H_2O$$

$$Cr(NO_3)_3+NaBiO_3+HNO_3 \rightarrow Na_2Cr_2O_7+NaNO_3+Bi(NO_3)_3+H_2O$$

31. Complete the following redox equations:

(a) $K_2Cr_2O_7+H_2S+H_2SO_4 \rightarrow \ldots$

(b) $Na_2CrO_4+KI+H_2SO_4 \rightarrow \ldots$

(c) $CrCl_3+H_2O_2+NaOH \rightarrow \ldots$

32. Employing the following scheme, write the chemical equations for the transition from chromate into dichromate and vice versa:

$$CrO_4^{2-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} Cr_2O_7^{2-}$$

33. If a piece of zinc is dipped into a potassium dichromate solution acidified with sulphuric acid, the solution turns green. Write down the respective equation for the reaction.

34. An iron vitriol solution was added to a potassium dichromate solution acidified with sulphuric acid. Write down the equation for the involved reaction.

35. Write down the equations for the reactions involved into the following transformations:

(a) $CrO_3 \rightarrow Cr_2O_3 \rightarrow Cr \rightarrow CrCl_3 \rightarrow Cr(OH)_3 \rightarrow NaCrO_2$

(b) $Cr \rightarrow Cr_2O_3 \rightarrow Cr_2(SO_4)_3 \rightarrow CrCl_3 \rightarrow KCrO_2 \rightarrow Cr(OH)_3$

36. How many kilograms of iron chromite containing 30% by mass of $Fe(CrO_2)_2$ will be required to prepare 200 kg of chromium, if the process follows the equation

$$Fe(CrO_2)_2+4C=2Cr+Fe+4CO?$$

37. 8 g of a compound were analyzed. It was found to contain 3.46 g of water of crystallization and 1.4 g of potassium sulphate. The rest amount was chromic sulphate. Determine the formula of the substance.

38. After a complete dehydration of 5.33 g of crystal hydrate of chromium chloride, water loss was 2.16 g. Derive the formula of the given crystal hydrate.

39. How many litres of chlorine are evolved when 1 mole of sodium dichromate is treated with an excess hydrochloric acid? Which chromium compound is produced in this reaction?

5.6 GROUP VIIB METALS

Metals manganese (Mn), technetium (Tc) and rhenium (Re) constitute Group VIIB.

Atoms of these metals have two electrons in their outermost electron shell and five electrons in the *d* orbitals of the penultimate electron shell. Therefore, manganese, technetium and rhenium can form compounds with valences varying from 1 to 7. However, compounds with valences of 1 and 5 are not typical and unstable for manganese and rhenium. For rhenium the most stable compounds have an oxidation number of +7, while for technetium compounds with oxidation number of +4, +6 and +7 are known.

A typical representative of Group VIIB is manganese. It is quite abundant and constitutes 0.03% of the total number of atoms in the earth's crust. Technetium, on the other hand, is unstable and has not been found in the earth's crust. It was prepared artificially as a result of nuclear transmutation reactions.

Rhenium, though found in the earth's crust, is an extremely rare element constituting only 9×10^{-9}%. Nevertheless rhenium and its derivatives are quite widely used in industry.

Example 1. What properties are exhibited by manganese dioxide? What do you know about the stability of the salts formed by the dioxide? How does MnO_2 react with oxidants? Can MnO_2 act as an oxidant?

Solution. MnO_2 exhibits amphoteric properties. However, compounds formed from this dioxide have weak basic and acidic properties:

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O$$

$$MnO_2 + 2KOH = K_2MnO_3 + H_2O$$

The manganese(IV) salts thus obtained are unstable and decompose on mild heating:

$$MnCl_4 = MnCl_2 + Cl_2$$

$$2K_2MnO_3 + O_2 = 2K_2MnO_4$$

When MnO_2 is fused with alkalies in the presence of oxidants manganates are formed:

$$MnO_2+2KOH+KNO_3=K_2MnO_4+KNO_2+H_2O$$

$$\begin{array}{rl|l} \text{Reductant} & \overset{+4}{Mn}-2e^-=\overset{+6}{Mn} & \times 1;\ \text{oxidation} \\ \text{Oxidant} & \overset{+5}{N}+2e^-=\overset{+3}{N} & \times 1;\ \text{reduction} \end{array}$$

In acid media MnO_2 acts as a reductant:

$$2MnO_2+3SnO_2+6HNO_3=2HMnO_4+3Sn(NO_3)_2+2H_2O$$

$$\begin{array}{rl|l} \text{Reductant} & \overset{+4}{Mn}-3e^-=\overset{+7}{Mn} & \times 2;\ \text{oxidation} \\ \text{Oxidant} & \overset{+4}{Sn}+2e^-=\overset{+2}{Sn} & \times 3;\ \text{reduction} \end{array}$$

In acid media MnO_2 is a strong oxidizing agent:

$$MnO_2+4HCl=MnCl_2+Cl_2+2H_2O$$

$$\begin{array}{rl|l} \text{Reductant} & 2\overset{-1}{Cl}-2e^-=\overset{0}{Cl_2} & \times 1;\ \text{oxidation} \\ \text{Oxidant} & \overset{+4}{Mn}+2e^-=\overset{+2}{Mn} & \times 1;\ \text{reduction} \end{array}$$

Example 2. Write down the reaction equations for the following conversions:

$$Mn \rightarrow MnSO_4 \rightarrow K_2MnO_4 \rightarrow MnO_2 \rightarrow MnO$$

Solution. 1. Mn readily dissolves in acids:

$$Mn+H_2SO_4\ (\text{dil.})=MnSO_4+H_2$$

or

$$Mn+2H_2SO_4\ (\text{conc.})=MnSO_4+SO_2+2H_2O$$

2. Divalent manganese salts exhibit reducing properties, viz. in acid media strong oxidants convert them into acids, H_2MnO_4 and $HMnO_4$, while in alkaline media into their salts:

$$MnSO_4+2KBrO+4KOH=K_2MnO_4+2KBr+K_2SO_4+2H_2O$$

$$\begin{array}{rl|l} & \overset{+2}{Mn}-4e^-=\overset{+6}{Mn} & \times 1 \\ & \overset{+1}{Br}+2e^-=\overset{-1}{Br} & \times 2 \end{array}$$

3. Potassium manganate disproportionates into potassium permanganate and manganese dioxide:

$$3K_2MnO_4+2H_2O=2KMnO_4+MnO_2+4KOH$$

$$\begin{array}{l|l} \overset{+6}{Mn}-1e^-=\overset{+7}{Mn} & \times 2 \\ \overset{+6}{Mn}+2e^-=\overset{+4}{Mn} & \times 1 \end{array}$$

4. The oxide with lower oxidation number, i.e. MnO, is obtained from oxides with higher oxidation number by reducing the latter:

$$MnO_2+H_2=MnO+H_2O$$

Example 3. Oxygen liberated during decomposition of potassium permanganate and measured at STP was all used for converting manganese dioxide into potassium manganate in an alkaline medium. Determine the masses of decomposed potassium permanganate and of the total amount of produced potassium manganate, if 50 ml of a potassium hydroxide solution which has a density of 1.2 g/ml and contains 22% by mass of KOH entered into the reaction.

Solution. Equations for the involved reactions are:

$$2KMnO_4 = K_2MnO_4+MnO_2+O_2 \qquad (1)$$

$$2MnO_2+4KOH+O_2 = 2K_2MnO_4+2H_2O \qquad (2)$$

$$\begin{array}{l|l} \overset{+4}{Mn}-2e^-=\overset{+6}{Mn} & \times 2 \\ \overset{0}{O_2}+4e^-=2\overset{-2}{O} & \times 1 \end{array}$$

Let us determine the mass of pure KOH that entered into the reaction: m = 50 ml × 1.2 g/ml = 60 g.

100 g of 22% KOH solution contain 22 g of KOH

60 g of 22% KOH solution contain

$$(60\ g \times 22\ g)/100\ g = 13.2\ g \text{ of KOH}$$

From Eq. (2) let us find the volume of oxygen that entered into the reaction and the mass of the produced potas-

sium manganate:

4×56 g of KOH need 22.4 litres of O_2

13.2 g of KOH need (13.2 g $\times$ 22.4 litres)/(4×56) g $= 1.32$ litres of O_2

4×56 g of KOH give 2×197 g of K_2MnO_4

13.2 g of KOH give (13.2 g $\times 2 \times 197$ g)/(4×56) g $= 23.2$ g of K_2MnO_4

Now let us find the masses of $KMnO_4$ and K_2MnO_4 from Eq. (1):

22.4 litres of O_2 come from 2×158 g of $KMnO_4$

1.32 litres of O_2 come from $\frac{1.32 \text{ litres} \times 2 \times 158 \text{ g}}{22.4 \text{ litres}}$ $= 18.6$ g of $KMnO_4$

2×158 g of $KMnO_4$ yield 197 g of K_2MnO_4

18.6 g of $KMnO_4$ yield (18.6 g $\times$ 197 g)/(2×158) g $= 11.6$ g of K_2MnO_4

Thus a total of 23.2 g + 11.6 g = 34.8 g of K_2MnO_4 was produced.

Therefore, the mass of the decomposed $KMnO_4$ is 18.6 g and that of the total amount of K_2MnO_4 is 34.8 g.

PROBLEMS AND EXERCISES

1. Which place does manganese occupy in the periodic table? What are the similarities and differences between this metal and the elements of the A subgroups.
2. Name the most abundant manganese minerals.
3. How can manganese be prepared in industry?
4. What is the valence of manganese in the following compounds: (a) K_2MnO_4, (b) $MnSO_4$, (c) $Ca(MnO_4)_2$, (d) $Mn(NO_3)_4$?
5. How do the properties of the manganese oxides change in the following series:

$$Mn \rightarrow Mn_2O_3 \rightarrow MnO_2 \rightarrow MnO_3 \rightarrow Mn_2O_7$$

Name the oxides.

6. Name the following hydroxides of manganese: $Mn(OH)_2$, $Mn(OH)_3$, $Mn(OH)_4$, H_2MnO_4, $HMnO_4$. Describe their properties.

7. Indicate the medium for a reaction between potassium permanganate and a reducing agent, if the solution (a) turned green, (b) became colourless, (c) turned brown.

8. Which oxidation states are the most characteristic of manganese?

9. What is the position of manganese in the electrochemical series? With which of the following salts will it react: (a) $SnSO_4$, (b) $MgCl_2$, (c) $Hg(NO_3)_2$, (d) $AuCl_3$?

10. Which of the following substances will react with manganese: (a) H_2O, (b) O_2, (c) KOH, (d) H_2SO_4, (e) H_2?

11. Which ions are there in the following manganese salt solutions: K_2MnO_3, $Ca(MnO_4)_2$, $Mn(NO_3)_2$, $NaMnO_4$?

12. Where are manganese and its compounds used?

13. Which of the two natural minerals, pyrolusite (MnO_2) or manganese spar (also called rhodochrosite, $MnCO_3$) contains more mass percent of manganese? Illustrate your answer with calculations.

14. Pure manganese is prepared by the electrolysis of aqueous solutions of manganese dichloride or manganese (II) sulphate. What processes take place at the cathode and at the anode during electrolysis of these salts when (a) a carbon anode, and (b) a manganese anode is used?

15. Technical-grade manganese can be prepared by the aluminothermic process according to the equation:

$$3Mn_3O_4 + 8Al = 9Mn + 4Al_2O_3 + 2500 \text{ kJ}$$

Write down the half-reaction equations for this redox reaction. How much manganese is formed and how much heat is evolved, if 45.8 g of Mn_3O_4 enter into the reaction?

16. Three methods, i.e. silicothermic, aluminothermic and electrolytic, are used for the preparation of metallic manganese. Illustrate these methods with chemical equations.

17. What volume of hydrogen will be evolved and how much manganese(II) hydroxide will be obtained by treating 15.5 g of manganese, containing 29% by mass of impurities insoluble in water, with water vapour?

18. Determine the oxidation numbers of manganese in the following manganese oxides: MnO_2, MnO_3, Mn_2O_3,

MnO, Mn_3O_4 and Mn_2O_7. Classify these oxides. Which regularity is exhibited with increasing oxygen valence of manganese?

19. Write the equation for the reaction between manganese(II) nitrate and lead dioxide in an acid medium, if the oxidized product is permanganic acid.

20. Write the equation for the reaction between manganese(II) sulphate and potassium chlorate in a neutral medium, if the oxidized product is manganic acid and the reduced one is gaseous chlorine.

21. Set up the equations for the reactions between potassium permanganate and (a) potassium nitrite in an alkaline medium, (b) potassium sulphite in a neutral medium, and (c) zinc in sulphuric acid.

22. In the presence of strong reductants, such as $NaNO_2$, the permanganate ion, MnO_4^-, is converted into Mn^{2+} ion in an acid medium; into MnO_4^{2-} in an alkaline medium; and into MnO_2 in a neutral medium. Write down the half-reaction and ionic equations for these reactions.

23. Write down the equations to represent the reactions in which MnO_2 exhibits (a) oxidizing properties, (b) reducing properties, (c) no change in the oxidation number.

24*. Manganese dioxide prepared by heating $Mn(NO_3)_2$ was dissolved in hydrochloric acid with heating. As a result, 2.24 litres of chlorine liberated. Nitrogen dioxide prepared by decomposition of $Mn(NO_3)_2$ was absorbed by 30 g of 40% KOH solution. Determine the mass of $Mn(NO_3)_2$ and the mass percents of substances in the solution prepared by dissolving NO_2 in the KOH solution (Cl_2 and NO_2 are measured at STP).

25. Balance the following equations using the ion-electron method:

$$K_2MnO_4+CO_2 \rightarrow KMnO_4+Mn_2O_3+K_2CO_3+O_2$$

$$K_2MnO_4+HNO_3 \rightarrow KMnO_4+MnO_2+KNO_3+H_2O$$

How are such redox reactions called?

26. Balance the following disproportionation reactions with the help of the ion-electron method:

$$Mn_2O_3+H_2SO_4 \rightarrow MnO_2+MnSO_4+H_2O$$

$$Mn_2O_3+HNO_3 \rightarrow MnO_2+Mn(NO_3)_2+H_2O$$

27. Write down the equations for the reactions involved in the following conversions:

$$Mn \rightarrow MnSO_4 \rightarrow H_2MnO_4 \rightarrow MnO_2 \rightarrow MnCl_2$$
$$Mn \rightarrow Mn(OH)_2 \rightarrow Mn(NO_3)_2 \rightarrow HMnO_4 \rightarrow MnO_2$$

28. Complete the following chemical equations in the molecular and ionic forms:

$$Mn_2O_3 + H^+ \rightarrow MnO_2 + \ldots$$
$$MnO_2 + OH^- + ? \rightarrow MnO_4^{3-} + \ldots$$
$$MnO_2 + H^+ + ? \rightarrow HMnO_4 + \ldots$$

29. Write down the following chemical equations in the molecular form

$$8MnO_4^- + 9H^+ + 5PH_3 = 8Mn^{2+} + 5PO_4^{3-} + 12H_2O$$
$$MnS + 8NO_3^- + 8H^+ = Mn^{2+} + SO_4^{2-} + 8NO_2 + 4H_2O$$
$$MnO_2 + 2H^+ + H_2O_2 = Mn^{2+} + O_2 + 2H_2O$$

30. How many grams of $KMnO_4$ will be required to oxidize 12.6 g of Na_2SO_3 in (a) an alkaline and (b) an acidic medium?

31. Why on mixing solutions of two soluble salts, $Mn(NO_3)_2$ and Na_2S no "flesh colour" precipitate of MnS is formed? Write down the equations for the involved reactions.

5.7 GROUP VIIIB METALS

The metals of Group VIIIB form three "triads". Iron (Fe), cobalt (Co), and nickel (Ni) belong to the first triad; ruthenium (Ru), rhodium (Rh), and palladium (Pd) constitute the second triad; while osmium (Os), iridium (Ir), and platinum (Pt) represent the third one. The first triad of elements is also called *iron family*, since iron, cobalt and nickel have similar properties that differ significantly from those of the rest. The elements of the second and third triads are said to belong to the *family of platinum metals* and have similar properties and abundance.

The outermost orbitals of these elements contain not more than two electrons. Hence, electron acception is not characteristic of them which reflects their metallic nature. The penultimate *d* orbitals of these elements are also

incomplete. This accounts for the formation of compounds with oxidation numbers varying from +2 to +8.

The characteristic oxidation number for Co and Ni is +2, while that for Fe is +3. Iron shows an additional oxidation number of +6, for cobalt it cannot be greater than +4 and nickel exhibits a formal additional oxidation number of +4.

The platinum family metals exhibit various oxidation numbers. The characteristic oxidation numbers of +2 and +4 are shown by platinum, of +3 and +4 by iridium, of +3 by rhodium and of +2 by palladium. The highest oxidation number (+8) is exhibited only by ruthenium and osmium in compounds like RuO_4 and OsO_4.

The ability to form complexes is a common property of all metals in Group VIIIB. Amongst the elements of iron family, iron is the most abundant metal.

Platinum family metals are less abundant and encountered nearly always together and mainly in native state, platinum being predominate.

Example 1. Iron is a quite active metal. Write down the equations for the reactions of iron with acids that are nonoxidants and with acids which are oxidants. How does iron react with salt solutions?

Solution. Dilute HCl and H_2SO_4 dissolve iron according to the equations:

$$Fe+2HCl=FeCl_2+H_2$$
$$Fe+H_2SO_4\ (dil.)=FeSO_4+H_2$$

Iron does not dissolve in concentrated H_2SO_4 under ordinary conditions; at elevated temperatures, however, the reaction proceeds as follows:

$$2Fe+6H_2SO_4=Fe_2(SO_4)_3+3SO_2+6H_2O$$

Dilute nitric acid (density 1.034 g/ml) dissolves iron at low temperatures:

$$4Fe+10HNO_3=4Fe(NO_3)_2+NH_4NO_3+3H_2O$$

When more concentrated nitric acid is used (density 1.073 g/ml) a mixture of ferrous and ferric nitrates is formed.

At low temperatures, concentrated HNO_3 as well as concentrated H_2SO_4, passivate iron because a firm protective film is formed on it. When iron is heated with con-

centrated nitric acid, the reaction equation is

$$Fe+4HNO_3=Fe(NO_3)_3+NO+2H_2O$$

It follows from the activity series for metals that iron can replace all metals that lie below it from their salt solutions to yield salts of divalent iron (also called ferrous salts):

$$Fe+Pb(NO_3)_2=Fe(NO_3)_2+Pb$$

Example 2. A mass of 4 g of a mixture of iron, ferrous and ferric oxides was reduced with hydrogen to yield a mass of 0.846 g of water. When the same amount of the mixture was treated with dilute sulphuric acid, 448 ml of hydrogen measured at STP were evolved. Calculate the mass percents of the components of the mixture.

Solution. 1. Since only iron reacts with acid to evolve hydrogen, let us determine the mass of iron in the mixture:

$$Fe+H_2SO_4=FeSO_4+H_2$$

22.4 litres of H_2 come from 56 g of Fe

0.448 litre of H_2 comes from

$$(0.448 \text{ litre} \times 56 \text{ g})/22.4 \text{ litres} = 1.12 \text{ g of Fe}$$

This means that the mixture contains $4 - 1.12 = 2.88$ g of oxides.

2. Let us now calculate the mass of each oxide in the mixture proceeding from the amount of water formed as a result of reduction of iron oxides by hydrogen:

$$FeO+H_2=Fe+H_2O$$

$$Fe_2O_3+3H_2=2Fe+3H_2O$$

Let X be the mass of ferrous oxide, then the mass of ferric oxide is $(2.88-X)$:

72 g of FeO yield 18 g of H_2O .

X g of FeO yields $18X/72$ g of H_2O

160 g of Fe_2O_3 produce 3×18 g of H_2O

$(2.88-X)$ g of Fe_2O_3 produce $(2.88-X) \times 3 \times 18/160$ g of H_2O

$$\text{But } \frac{18X}{72}+\frac{(2.88-X)\times 3\times 18}{160}=0.846$$

whence $X = 1.44$ g and $(2.88 - X) = 1.44$ g.

Thus, the mixture contains 1.44 g each of FeO and Fe_2O_3.

3. We can now calculate the mass percent of iron in the mixture:

4 g of the mixture constitute 100%

1.12 g of the mixture constitite

$$(1.12\ g \times 100\%)/4\ g = 28\%$$

4. Likewise, the mass percents of FeO and Fe_2O_3 are ound as follows:

4 g of the mixture are 100%

1.44 g of the mixture are $(1.44\ g \times 100\%)/4\ g = 36\%$

Therefore, the given mixture consists of 28% Fe, 36% FeO and 36% Fe_2O_3.

PROBLEMS AND EXERCISES

1. Which place in the periodic table does iron occupy?
2. In which form does iron occur in nature? Name the most important naturally occurring compounds of iron.
3. How will you prepare iron in the laboratory?
4. What are the characteristic oxidation numbers of iron?
5. Determine the oxidation numbers of iron in the following compounds: $KFe(SO_4)_2$, $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, and $BaFeO_4$.
6. How is iron obtained from iron ores?
7. What is cast or pig iron? How does it differ from steel?
8. List the methods of preparation of steel, their advantages and drawbacks.
9. With which of the following solutions will iron react: KOH, H_3PO_4, $AgNO_3$, $MgCl_2$, KSCN? Justify your answer.
10. With which of the following substances will ferric oxide react: H_2O, HCl, NaOH, $CuCl_2$?
11. Indicate the substances, with which ferric hydroxide will react: HNO_3, KOH, $ZnSO_4$, H_2CO_3.
12. Which oxides and hydroxides are formed by iron?
13. In what way do iron, cobalt and nickel resemble one another?

14. What types of corrosion do you know? In what way do they differ from one another?

15. Why does iron corrode in moist air?

16. What is the difference between corrosion of iron in acid media and in neutral media?

17. Explain the operation of a galvanic cell.

18. What is the nature of electrochemical corrosion?

19. Name the methods employed for corrosion protection.

20. Does tin act as an anode or cathode protection (a) for zinc, (b) for copper?

21. How does corrosion proceed in the case of galvanized iron, if the zinc layer is destroyed?

22. Determine the mass percents of iron in its natural compounds: siderite, $FeCO_3$; iron pyrite, FeS_2; limonite or brown hematite, $Fe_2O_3 \cdot H_2O$.

23. Magnetite consists of a mixed oxide, Fe_3O_4. How many atoms of divalent and trivalent iron, respectively, are there in one molecule of this oxide? Determine the mass percent of iron in this compound.

24. Which reactions underlie iron smelting in a blast furnace?

25. How many tons of cast iron can be smelted from 100 tons of hematite containing 65 mass percent of ferric oxide?

26. One of the iron oxides contains 22.2% by mass of oxygen. Determine the equivalent of iron and the formula of the given oxide.

27. How many kilograms of iron may be reduced by aluminium from 3 kg of ferric oxide containing 10 mass percent of impurities?

28. What happens to iron when it is treated with water, oxygen or carbon dioxide? Write down the reaction equations.

29. What mass of 20% HCl is required in order to dissolve 7.4 g of iron?

30. What volume of 2 *M* hydrochloric acid solution is required to dissolve 0.56 g of iron?

31. When dissolved in hot nitric acid which has a density of 1.4 g/ml and contains 65% by mass of HNO_3, a mass of 9.5 g of a mixture of iron and gold liberated 2.8 litres of nitrogen(II) oxide. Determine the mass percent

of iron in the mixture and the volume of the consumed acid.

32. Write down the structural (graphic) formulas and determine the oxidation numbers for iron in the following compounds: FeS_2, K_2FeO_4, $(FeOH)_2CO_3$ and $FeHPO_4$.

33. Write down the molecular and ionic equations for the reactions involved in the following conversions:

(a) $Fe \rightarrow FeCl_2 \rightarrow FeCl_3 \rightarrow Fe(OH)_3 \rightarrow Fe_2O_3$

(b) $Fe \rightarrow Fe_2(SO_4)_3 \rightarrow FeCl_3 \rightarrow Fe(NO_3)_3 \rightarrow Fe_2O_3$

(c) $Fe \rightarrow Fe(NO_3)_2 \rightarrow Fe \rightarrow Fe(NO_3)_3 \rightarrow Fe_2O_3 \rightarrow Fe$

34. Set up the molecular and ionic equations for the following reactions:

(a) $FeSO_4 + K_3[Fe(CN)_6] \rightarrow \ldots$

(b) $FeCl_3 + K_4[Fe(CN)_6] \rightarrow \ldots$

35. Write down the molecular and ionic equations for the hydrolysis of the following iron salts: $Fe_2(SO_4)_3$, Fe_2S_3, $Fe(NO_3)_3$ and $Fe(CH_3COO)_3$. When solutions of $FeCl_3$ and K_2CO_3 are mixed, CO_2 is liberated and $Fe(OH)_3$ precipitates. Why?

36. What properties do ferrous and ferric compounds exhibit in the following redox reactions:

(a) $Fe_2S_3 + HCl \rightarrow FeCl_2 + H_2 + S$

(b) $FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O$

(c) $Fe(OH)_3 + KOH + 3Br_2 \rightarrow K_2FeO_4 + KBr + H_2O$

Balance the above redox equations.

37. How are Berlin blue and Turnbull's blue (insoluble Prussian blue) prepared? Write the respective reaction equations.

38*. When 9 g of an alloy of iron, copper and aluminium were dissolved in hydrochloric acid, 5.6 litres of hydrogen measured at STP were evolved and 0.7 g of undissolved residue remained. Determine the mass percents of the metals in the alloy.

39. When a 6-g sample of cast iron was treated with hydrochloric acid, a volume of 2.24 litres of a gas measured at STP was liberated. Determine the mass percent of iron in the sample. How many millilitres of 18.25% HCl (density 1.09 g/ml) entered into the reaction?

40. A mixture of zinc and iron which contains 5.6 g of iron is treated with hydrochloric acid which has a density of 1.1 g/ml and contains 20% by mass of HCl. As a result, 13.44 litres of a gas (STP) are evolved. What is the mass of the mixture? What volume of acid is used.

41*. A volume of 66.36 ml of hydrochloric acid of density 1.1 g/ml and containing 20% by mass of HCl is used for dissolving 12.8 g of a mixture of metallic iron and ferrous oxide. To completely oxidize this ferrous oxide the whole of oxygen is used that liberated during decomposition of 2.042 g of potassium chlorate (Berthollet's salt). Determine the mass percents of iron and ferrous oxide in the mixture.

42*. A mass of 7.25 g of a mixture of FeO and Fe_2O_3 is reduced by carbon monoxide. The produced carbon dioxide is absorbed by 2.5 *M* sodium hydroxide solution of density 1.10 g/ml. What is the smallest volume of NaOH solution that is required to absorb the produced carbon dioxide? Determine the mass percent of the obtained salt in the final solution.

43*. When 1 g of a mixture of Fe and Fe_3O_4 was dissolved in hydrochloric acid, 0.224 litre of hydrogen measured at standard conditions was evolved. How much water will be obtained if Fe_3O_4, contained in 3 g of the mixture, is reduced?

44*. 4 g of a mixture of iron, ferrous oxide and ferric oxide were reduced with hydrogen to yield 0.846 g of water. When this mixture was treated with dilute sulphuric acid, 448 ml of hydrogen measured at STP were liberated. Determine the mass percents of iron and the two oxides in the mixture.

45*. Iron produced from 11.7 g of ferric oxide by the aluminothermic method entered into reaction with chlorine evolved during electrolysis of a sodium chloride solution. How many millilitres of 21% NaCl solution (density 1.17 g/ml) should be taken for the electrolysis in order to chlorinate the whole amount of iron? What is the volume of chlorine that entered into the reaction with iron?

46*. An iron plate with a mass of 40 g was dipped into a copper salt solution, then washed with water and dried. The mass of the plate was found to be 41.6 g. How

much metallic copper was deposited on the iron plate from the solution? How many millilitres of nitric acid having a density of 1.5 g/ml and containing 96% by mass of HNO_3 are to be used to remove the copper coating from the plate?

47. Calculate the mass of iron that may be obtained from magnetite, Fe_3O_4, by reacting it with 144 g of aluminium.

48. How many litres of hydrogen are required in order to reduce iron from hematite, Fe_2O_3, if 1.12 g of iron are formed?

49. In the manufacture of steel, ferrous oxide oxidizes impurities such as silicon, phosphorus and carbon present in the melt. How many kilograms of the oxidation products are formed, if the melt contains 2.8 kg of silicon, 3.01 kg of phosphorus and 1.2 kg of carbon?

50. A mixture of iron and copper was treated with a hydrochloric acid solution having a density 1.1 g/ml and containing 20% by mass of HCl. The mixture contains 35 mass percent of iron. Calculate the mass of the original mixture, if as a result of the reaction, 244 ml of a gass measured at STP are evolved. Also calculate the volume of the acid that entered into the reaction.

51. 27.2 g of a mixture of iron and ferrous oxide were treated with sulphuric acid and subsequently evaporated to yield 111.2 g of $FeSO_4 \cdot 7H_2O$. Calculate the mass percents of iron and iron oxide in the mixture.

52. Calculate the masses of cupric sulphate and ferrous sulphate in 1.202 g of their mixture, if 1.086 g of a precipitate were formed when an excess barium chloride solution was added to the mixture.

53. Calculate the volume of 2 *M* hydrochloric acid solution required to dissolve 0.56 g of iron.

54. Calculate the volume of 0.5 *M* sodium hydroxide solution that is needed for reacting with 20 ml of 0.1 *M* ferric chloride solution.

55. How much ferric chloride is required in order to prepare 4.3 g of silver chloride?

56. Calculate the equivalent of iron, if it is known that 22.4 g of iron react with chlorine to yield 65 g of the respective chloride.

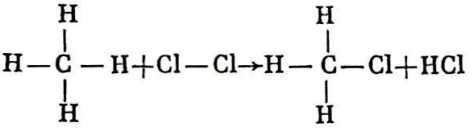
6
HYDROCARBONS

6.1 SATURATED HYDROCARBONS (PARAFFINS, ALKANES)

The molecules of saturated hydrocarbons contain carbon atoms attached to one another by single bonds and bonded to hydrogen atoms also by single bonds to saturate the carbon valences.

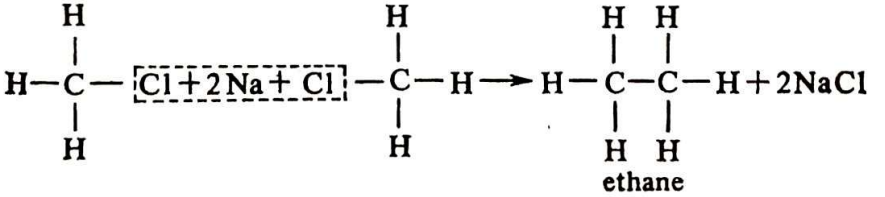
The simplest representative of the saturated hydrocarbons is *methane*, CH_4. Several groups of organic compounds may be united into homologous series. Each member of homologous series differs from the preceding one by a $-CH_2-$ group (methylene group) known as a homologous difference.

The homologous series of methane. If methane is treated with chlorine, then a haloderivative, methyl chloride, is formed:



methane — methyl chloride

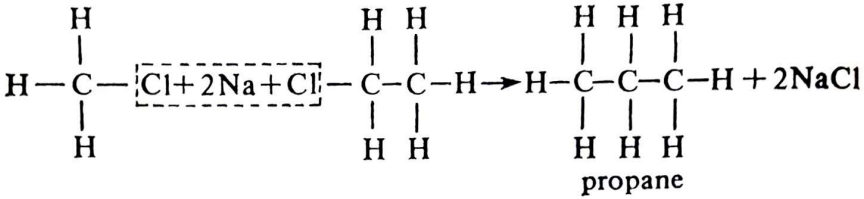
Two molecules of methyl chloride in the presence of metallic sodium yield another saturated hydrocarbon, *ethane* (Wurtz reaction):



ethane

If a mixture of haloderivatives of methane and ethane is treated with metallic sodium, the hydrocarbon *propane*

is formed:



In this way, one can prepare the other saturated hydrocarbons of this series. Hydrocarbons which follow propane are butane (C_4H_{10}), pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), octane (C_8H_{18}), and so on.

The first four members of the saturated hydrocarbon series have been given trivial names. Starting with C_5H_{12}, their names are derived from the respective Greek numerals. Only in a few cases are Latin names used.

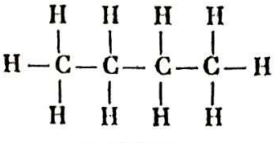
If the number of carbon atoms is denoted by n, then the number of hydrogen atoms bonded to this carbon will be $2n + 2$, and hence the general formula for the saturated hydrocarbons is C_nH_{2n+2}. For example, in nonane the number of carbon atoms equals 9, and the number of hydrogen atoms is, according to the formula, equal to 20.

Isomerism and nomenclature. If one hydrogen atom is removed from a molecule of any saturated hydrocarbon, the residual part of the molecule is known as a *hydrocarbon radical*. The names of monovalent hydrocarbon radicals are formed from the names of the respective saturated hydrocarbons by replacing the suffix 'ane', with the suffix 'yl' as illustrated below:

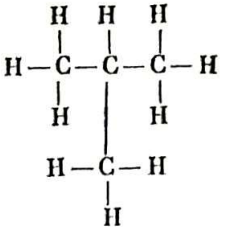
CH_4 methane	$-CH_3$ methyl
C_2H_6 ethane	$-C_2H_5$ ethyl
C_3H_8 propane	$-C_3H_7$ propyl

These radicals have a common name of *alkyls*, whence another name for the saturated hydrocarbon is *alkanes*.

Beginning with butane the saturated hydrocarbons can have different structures:



n-butane

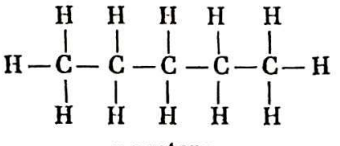


isobutane

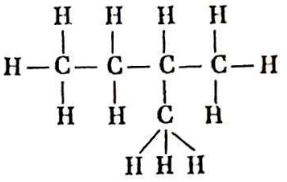
In *n*-butane all carbon atoms are bonded to one another to form a straight chain, while in isobutane there is a branching (side chain).

Compounds with the same composition and molecular mass but different structural formulas are called *isomers*. In the above example, butane can have two possible structures (isomers). One of these two isomers has an unbranched chain of carbon atoms and is called *normal butane* (*n*-butane for short), whereas the other is with a branched chain and is known as *isobutane*.

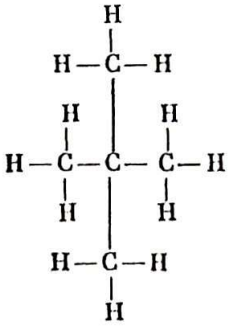
Likewise, the following three isomers are possible for pentane:



n-pentane



isopentane



neopentane

The hydrocarbon $C_{10}H_{22}$ has 75 isomers, $C_{20}H_{42}$ has 366319 isomers while $C_{40}H_{82}$ has a 14-digit number of isomers.

Bulky structural formulas cannot be handled conveniently. This is why such formulas are represented in the condensed form as shown below for the isomers of pentane:

$CH_3-CH_2-CH_2-CH_2-CH_3$ or $CH_3CH_2CH_2CH_2CH_3$

n-pentane

$CH_3-CH_2-CH(CH_3)-CH_3$ or $CH_3CH_2CH(CH_3)CH_3$

isopentane

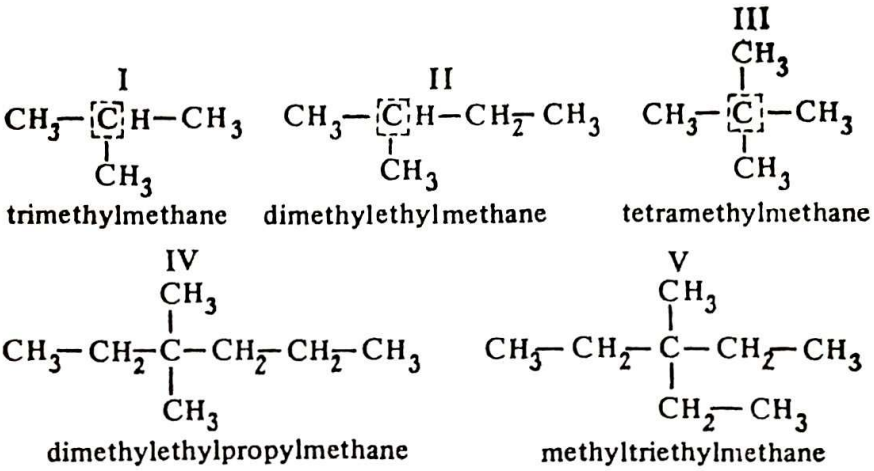
$CH_3-C(CH_3)_2-CH_3$ or $CH_3C(CH_3)_2CH_3$

neopentane

Obviously, two hydrocarbons with different structural formulas cannot have the same name. For this reason, three systems of nomenclature, viz. rational, Geneva and IUPAC systems are used nowadays to completely describe the composition and structure of organic compounds having branched-chain isomers.

The *rational* (semisystematic or semitrivial) nomenclature for saturated hydrocarbons considers the latter as the derivatives of methane, in which one or several hydrogen atoms are replaced by hyrocarbon radicals or alkyl groups. For this reason, that carbon atom is chosen which has the largest number of substituents (radicals). These radicals are indicated in the order of increasing carbon atoms. If several identical substituents are present, Greek numerals such as di (for two), tri (for three), tetra (for four), penta (for five), etc., are used as prefixes.

For example:



The more complex the formula, the more difficult it is to name it according to the rational nomenclature and sometimes even impossible. This is why the Geneva and IUPAC nomenclatures are most often used.

The *Geneva nomenclature* was adopted in 1892 in Geneva by the International Conference of Chemists (whence the name of the nomenclature). Nearly 40 years later, different boards of chemists have worked out a set of rules which was introduced in 1957 as a new IUPAC (for International Union of Pure and Applied Chemistry) nomenclature. These rules are basically the same as those used in the Geneva nomenclature, the only difference being that this new system simplifies the naming of the simplest radicals in a side chain.

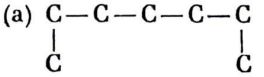
For naming a hydrocarbon (for other classes of organic compounds this nomenclature is similar in many respects) in the *IUPAC nomenclature*, first the longest carbon chain is chosen which is then numbered in such a way that the substituents get the lowest number. Next, the position of each substituent is indicated by a separate numeral. When different substituents are present, their names are alphabetically arranged. The name of the hydrocarbon corresponding to the longest carbon chain is given at the end. If the side chain contains several iden-

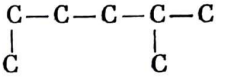
tical radicals, the prefixes di, tri, tetra, etc., are employed to indicate the number of such radicals, while the position of each radical is indicated by an individual numeral.

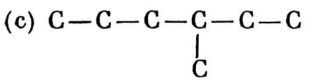
The structural formulas I-V presented above have the following IUPAC names: 2-methylpropane (compound I), 2-methylbutane (compound II), 2,2-dimethylpropane (compound III), 3,3-dimethylhexane (compound IV), and 3-ethyl-3-methylpentane (compound V).

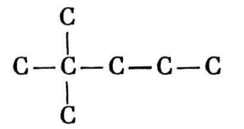
Depending upon how complex organic compounds are, in the present discussion we shall give them rational and/or IUPAC names, and in a few cases only shall we use trivial names.

Example 1. Which of the following carbon skeletons corresponds to the compound whose name starts with the prefix iso?

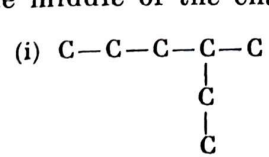
(a) 

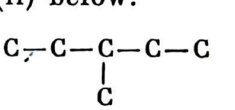
(b) 

(c) 

(d) 

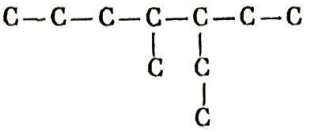
Solution. Skeleton (b) corresponds to an iso-compound, since such a compound should have a one-carbon branching at the penultimate atom of the long carbon chain. Straightening out the bending we get the skeleton formula C—C—C—C—C—C. Skeleton (a) may be written as a straight chain C—C—C—C—C—C—C as well as with any type of bending. Skeleton (c) represents either a two-carbon branching at the penultimate carbon atom of the chain as shown in (i) below or a one-carbon branching at the middle of the chain as in (ii) below:

(i) 

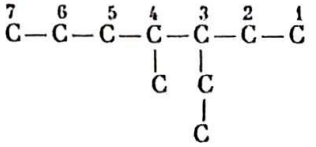
(ii) 

Skeleton (d) is not an iso-compound because the penultimate carbon atom of the long chain has two branchings.

Example 2. Name the saturated hydrocarbon which has the following carbon skeleton:

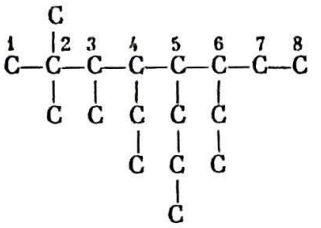


Solution. In this compound numbering is determined by ethyl as it is nearest to one end of the carbon chain (locant); this radical has the numerical 3, while methyl group is attached to the carbon No. 4. Alphabetically these two groups should be arranged in this order:



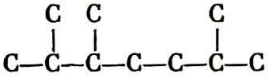
3-ethyl-4-methylheptane

Example 3. Name the alkane having the following carbon skeleton:



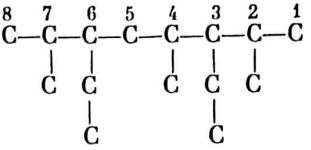
Solution. 4,6-Diethyl-2,2,3-trimethyl-5-propyloctane.

Example 4. Name the alkane of the following carbon skeleton:



Solution. In this case two identical substituents are at the same distance from the terminal carbon atoms. Hence, the given compound may be named either as 2,3,6-trimethylheptane or as 2,5,6-trimethylheptane. Amongst these two names the first one is correct, since $(2 + 3 + 6) < (2 + 5 + 6)$.

Example 5. Name the following alkane:



Solution. 3,6-Diethyl-2,4,7-trimethyloctane.

Example 6. Natural gas contains 85% methane, 6% ethane, 3% carbon monoxide, 4.5% carbon dioxide, 1.5% nitrogen and inert gases together (all by volume). What volume of air is required to burn 1 m^3 of this gas? The volume percent of oxygen in the air constitutes 21%.

Solution. 1m^3 of the given natural gas contains 850 litres of methane, 60 litres of ethane and 30 litres of carbon monoxide. The remaining gases do not participate in the combustion reactions.

The volume of oxygen required to burn 850 litres of methane is

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

1 volume of CH_4 needs 2 volumes of O_2

850 litres of CH_4 need $(850 \times 2)/1 = 1700$ litres $= 1.7$ m^3 of O_2

The volume of oxygen needed to burn 60 litres of ethane:

$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O$$

1 volume of C_2H_6 needs 3.5 volumes of O_2

60 litres of C_2H_6 need $(60 \times 3.5)/1 = 210$ litres $= 0.21$ m^3 of O_2

The volume of oxygen needed to burn 30 litres of carbon monoxide may likewise be calculated on the basis of the following equation:

$$2CO + O_2 = 2CO_2$$

2 volumes of CO need 1 volume of O_2

30 litres of CO need $(30 \times 1)/2 = 15$ litres $= 0.015$ m^3 of O_2

In this way, a total of $1.7 + 0.21 + 0.015 = 1.925$ m^3 of O_2 is required to burn the given volume of natural gas.

Now 1 m^3 of air contains 210 litres (0.21 m^3) of oxygen. We can, therefore, calculate the volume of air needed to burn the given natural gas:

0.21 m^3 of O_2 is in 1 m^3 of air

1.925 m^3 of O_2 are in (1.925 $m^3 \times 1$ m^3)/0.21 m^3

$= 9.17$ m^3 of air

Example 7. A volume of 2.24 litres of a gaseous hydrocarbon was burnt in oxygen to yield 13.2 g of carbon dioxide and 7.2 g of water according to the following equations:

$$C + O_2 = CO_2 \quad 2H_2 + O_2 = 2H_2O$$

The hydrocarbon has a density of 1.52 with respect to air at STP. Derive the molecular formula of the gaseous hydrocarbon.

Solution. The molecular mass of the gas is:

$$M = 29 \times D_{air} = 29 \times 1.52 = 44$$

Now let us calculate the masses of carbon and hydrogen in 2.24 litres of the given hydrocarbon:

44 g of CO_2 come from 12 g of carbon

13.2 g of CO_2 come from (13.2 g $\times$ 12 g)/44 g $= 3.6$ g of C

36 g of H_2O come from 4 g of hydrogen

7.2 g of H_2O come from (7.2 g $\times$ 4 g)/36 g $= 0.8$ g of H

This means that the sum total of carbon and hydrogen in the burnt gas is 3.6 g + 0.8 g = 4.4 g. We shall calculate now the mass of 2.24 litres of the hydrocarbon:

22.4 litres weigh 44 g

2.24 litres weigh (2.24 litres $\times$ 44 g)/22.4 litres $= 4.4$ g

Therefore, the given gas contains carbon and hydrogen only.

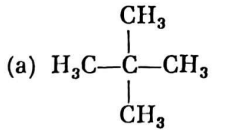
$$C : H = \frac{3.6}{12} : \frac{0.8}{1} = 0.3 : 0.8 = 1 : 2.66$$

Hence the simplest (empirical) formula is $CH_{2.66}$ for which $M_r = 14.66$. Now the ratio between the masses of the true (molecular) formula and the simplest (empiri-

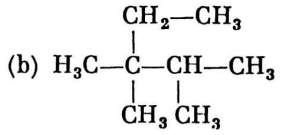
cal) one is $44/14.66 = 3$. This means that the simplest formula is to be increased thrice in order to obtain the molecular formula. The molecular formula is thus $(CH_{2.66})_3 = C_3H_8$.

PROBLEMS AND EXERCISES

1. Which organic compounds belong to the hydrocarbon series?
2. Which hydrocarbons are called saturated?
3. What is a homologous series? What is a homologous difference?
4. Name the saturated hydrocarbons containing one to ten carbon atoms.
5. Which of the following hydrocarbons are saturated: C_6H_{14}, C_2H_4, $C_{10}H_{22}$, C_3H_8, $C_{20}H_{42}$, and C_6H_6?
6. Can the following compounds have isomers: methane, ethane, and propane?
7. Why are saturated hydrocarbons called (a) saturated, (b) alkanes, (c) paraffins?
8. Which electrons take part in the formation of chemical bonds in the molecules of CH_4, C_2H_6, and C_4H_{10}?
9. Why do the molecules of saturated hydrocarbons contain even number of hydrogen atoms?
10. Which alkanes and their derivatives are encountered in everyday life?
11. Name the following saturated hydrocarbons according to the rational nomenclature:



(a)



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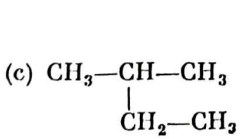

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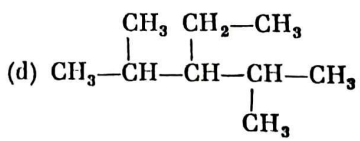
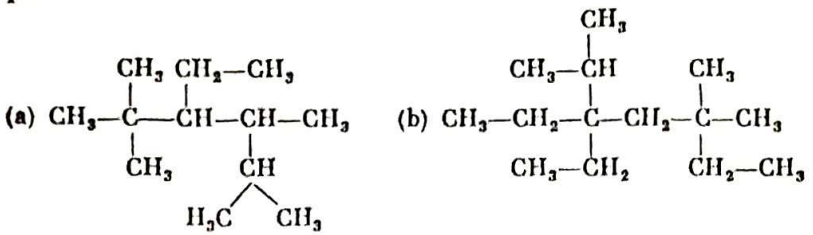


(d)

12*. Write the IUPAC names for the following compounds:



13. Which hydrocarbons are formed when the following haloderivatives are treated with metallic sodium: (a) bromoethane, (b) 1-bromopropane, (c) 2-chloropropane, (d) 1-chloro-2-methylpropane?

14. Write the empirical and structural formulas for the first five (C_1 to C_5) saturated hydrocarbons with unbranched carbon atom chains.

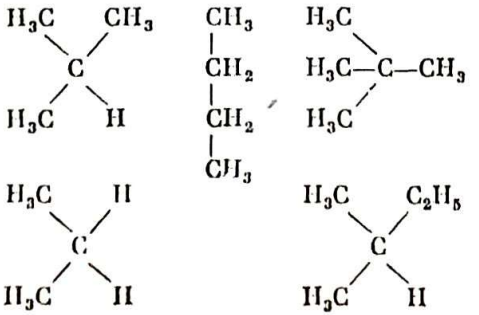
15. Write the formulas for the following radicals (alkyl groups): methyl, ethyl, butyl, and amyl.

16. Write the structural formulas for all the possible isomers of pentane. Name each of these isomers according to the (a) rational, and (b) Geneva nomenclature.

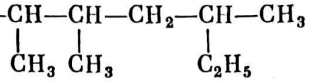
17. Write the structural formulas and names in the IUPAC nomenclature for the following paraffins: (a) trimethylethylmethane, (b) dimethyldiethylmethane, (c) methyldiethylisopropylmethane, (d) dimethyldiisopropylmethane, and (e) triisopropylmethane.

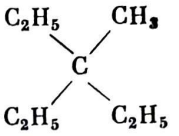
18. Write the structural formulas and the rational names for the following alkanes: (a) 2,3-dimethylpentane, (b) 3-ethyl-3-methylpentane, (c) 2-isopropyl-2,3,4-trimethylpentane, (d) 2,2,4,4-tetramethylpentane, (e) 3,3-diethyl-2,4-dimethylpentane.

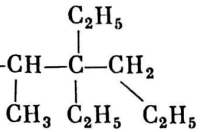
19. Name each of the following compounds according to the rational and IUPAC nomenclatures:

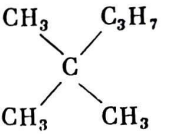


20. Indicate the longest carbon chain in the following hydrocarbons, write them down horizontally and name by the IUPAC nomenclature:

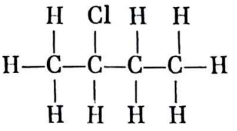
(a) 

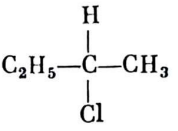
(b) 

(c) 

(d) 

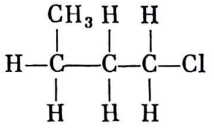
21. Which of the following compounds are isomers?

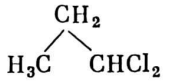




$CH_3—CH_2CHCl_2$

$CH_2ClCH_2CH_2Cl$





Name them by the rational and IUPAC nomenclatures.

22. Which of the following compounds may have isomers: $C_3H_6Cl_2$, CH_2Cl_2, $C_2H_4Cl_2$, and $C_2H_5CHCl_2$? Name all these compounds by the rational nomenclature. Give structural formulas to support your answer.

23. Write the equations for the reactions of stepwise oxidation of methane by bromine and name all the bromo derivatives thus produced.

24. How will you prepare propane and butane from the following substances: methane, metallic sodium and chlorine? Mention the reaction conditions.

25. What volume of methane will be liberated (a) when 72 g of Al_4C_3 is hydrolyzed; (b) from 4.1 g of anhydrous sodium acetate?

26. Which hydrocarbons are formed when the following salts of carboxylic acids are heated with solid sodium

hydroxide?

(a) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-COONa$ (b) $CH_3-\underset{\displaystyle CH_3-CH_2}{\underset{|}{CH}}-CH_2-COONa$

27. Which reactions can be used for the following conversions:

(a) $CH_4 \rightarrow CH_3Cl \rightarrow C_2H_6 \rightarrow C_2H_5Cl \rightarrow C_3H_8$

(b) $C \rightarrow CH_4 \rightarrow CH_3Cl \rightarrow C_3H_8 \rightarrow C_3H_7Br$

28. Derive the molecular formula of a substance which contains 85.7% by mass of carbon and 14.3% by mass of hydrogen. It has a vapour density of 21 with respect to hydrogen.

29. Derive the formula of a compound which contains 81.8% by mass of carbon and 18.2% by mass of hydrogen.

30. A substance contains 83.72 mass percent of carbon and 16.28 mass percent of hydrogen and has a molecular mass of 86. Derive the molecular formula of the substance.

31. Calculate the density of ethane with respect to (a) air and (b) hydrogen.

32. How much oxygen is required to burn (a) 4 g of methane, (b) 0.1 mole of methane, (c) 10 litres of methane?

33. What volume of hydrogen is formed as a result of conversion of 10 m^3 of methane by water vapour (steam)?

34. Determine the mass of carbon black produced when 20 m^3 of methane are pyrolyzed.

35. How many cubic metres of oxygen measured at STP will be required to burn 2 m^3 of a gaseous mixture containing 75% methane, 15% ethane and 5% hydrogen (all by mass)?

36*. Combustion of a compound containing carbon, hydrogen and chlorine yields 13.2 g of CO_2 and 6.3 g of H_2O. When the same amount of this compound was taken for chlorine determination, 14.35 g of silver chloride were obtained. The compound has a vapour density of 2.707 with respect to air. Derive the formula of this compound.

37. What volume of air is required for complete combustion of one litre of methane at standard conditions?

38. What volume of air is needed to burn 2 m^3 of natural gas that contains 90% methane, 5% ethane, 3% carbon dioxide and 2% nitrogen (all by mass)?

39. What is the mass of 1 litre of pentane at standard conditions?

40. One litre of a gas has a mass of 2.58 g at standard conditions. Calculate its relative molecular mass and density with respect to air.

41. Write the formula of a methane homologue which when burnt produces five times as much carbon dioxide as methane does.

42. What volume of methane will be needed for a reaction with 1 litre of chlorine at standard conditions to yield methyl chloride?

43. Write the formula of a methane homologue if it is known that 5.6 litres of this homologue weigh 11 g at standard conditions.

44. How many grams of methyl chloride are formed when 10 litres of methane measured at standard conditions are chlorinated?

45. Determine the carbon contents in 1 m^3 of natural gas consisting of 92% by mass of methane, 4% by mass of ethane and incombustible impurities.

46. Derive the molecular formula of a gaseous substance from the following data: it has a vapour density of 2 with respect to air and contains 82.76% C and 17.24% H (by mass).

47. Combustion of a gaseous hydrocarbon yielded 3.3 g of carbon dioxide and 2.02 g of water. Write the structural formula of the hydrocarbon, if its vapour density with respect to air is 1.04.

48. Three moles of sodium acetate can produce (a) how many moles of methane, (b) how many grams of methane, (c) how many litres of methane at STP?

49. An explosive mixture of methane and air contains 5 to 15 mass percent of methane. Calculate the masses of methane in 1 m^3 of the mixture for the minimum and maximum explosion ranges.

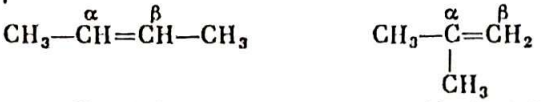
6.2 UNSATURATED HYDROCARBONS

The molecules of unsaturated hydrocarbons contain unsaturated carbon-carbon bonds, that is, contain multiple carbon-carbon bonds such as double and triple bonds.

Unsaturated hydrocarbons containing one double bond

*are called alkenes (ethylenic hydrocarbons, olefins).** The homologous series of ethylene hydrocarbons has the general formula C_nH_{2n}.

Nomenclature of ethylenic hydrocarbons. Names of the ethylenic hydrocarbons according to the rational nomenclature are derived from those of the respective saturated hydrocarbons by replacing the '*ane*' by '*ylene*'. The rational nomenclature often considers the olefins as the derivatives of ethylene, in which one or several hydrogen atoms has been replaced by alkyl groups. The positions of these alkyl groups bonded to different carbon atoms in an ethylene skeleton are denoted by Greek letters α and β:

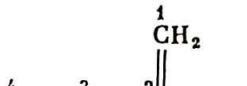


symm-dimethylethylene or α, β-dimethylethylene

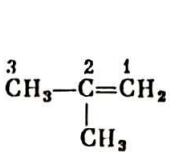
nonsymm-dimethylethylene or α, α-dimethylethylene

In the IUPAC nomenclature the suffix '*ane*' in the saturated hydrocarbons is replaced by 'ene' in the unsaturated ethylenic hydrocarbons. The carbon chain containing the double bond (even though it is not the longest one) is taken as the parent hydrocarbon. The carbon atoms in such a chain are numbered from that end, which is nearer so the double bond. A numerical prefix is used to indicate the position of the double bond in the carbon chain. For example:

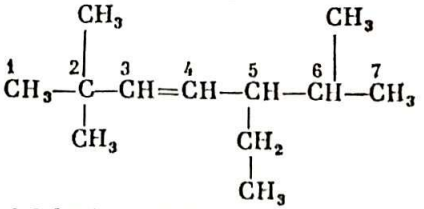
1-butene



2-methyl-1-butene



2-methyl-1-propene



2,2,6-trimethyl-5-ethyl-3-heptene or, 5-isopropyl-2,2-dimethyl-3-heptene

* The use of the term olefins (a Latin word which means olefiant gas) is explained by the fact that the halogen derivatives of this series represent oily substances.

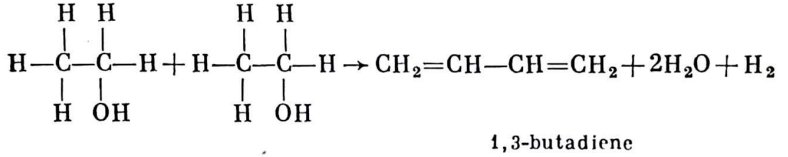
Unsaturated hydrocarbons containing two double bonds are called alkadienes.

The two double bonds in alkadiene molecules may be arranged in different ways. These may be arranged either at a single carbon atom (=C=) forming thus the so-called cumulated double bonds, or may be separated by a single bond (—C=C—C=C—), which gives rise to a conjugate double bond.

Let us consider a few representatives containing conjugate double bonds. A specific feature of the hydrocarbons in this series is that they can readily polymerize. These polymers resemble natural rubber in many properties.

Rubber synthesis by the S.V. Lebedev method consisted of two steps:

1. Preparation of butadiene from ethyl alcohol in the presence of catalysts such as Al_2O_3 and ZnO:



$$2\,C_2H_5OH \rightarrow CH_2=CH-CH=CH_2 + 2H_2O + H_2$$

1,3-butadiene

2. Polymerization of butadiene in the presence of metallic sodium:

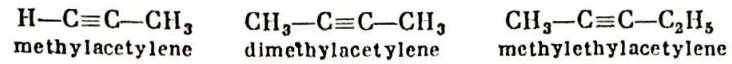
$$\ldots -CH_2=CH-CH=CH_2 + CH_2=CH-CH=CH_2 + \ldots \rightarrow$$
$$\rightarrow \ldots -CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2- \ldots$$

Nowadays butadiene is prepared by the pyrolysis of petroleum fractions. During pyrolysis, benzenes and other liquid hydrocarbons obtained from petroleum yield hydrocarbons containing four carbon atoms (*n*-butylene, isobutane, butadiene) along with ethylene and propylene.

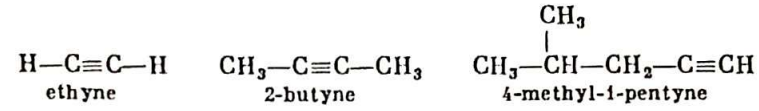
Unsaturated hydrocarbons containing triple bonds are called alkynes.

The simplest member of the alkyne series is acetylene, C_2H_2 or H—C≡C—H. Other members of the homologous series of hydrocarbons containing one triple bond can be prepared by successively replacing hydrogen atoms from an acetylene molecule. Their general molecular formula is C_nH_{2n-2}. Names of the alkynes are formed in the same way as it was done for naming alkanes.

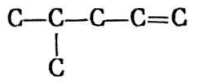
According to the rational nomenclature, the alkynes are considered to be the derivatives of acetylene in which one or both hydrogen atoms are replaced by alkyl radicals:



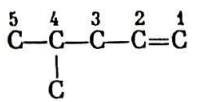
In the IUPAC system acetylene hydrocarbons are named by replacing the suffix 'ane' in the respective alkanes by the suffix 'yne' and indicating the position of the triple bond by a numeral as shown below:



Example 1. Name the following unsaturated hydrocarbon containing one double bond according to the IUPAC nomenclature:

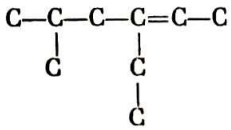


Solution. Alkenes derive their names from those of the corresponding alkanes by replacing the suffix 'ane' by 'ene'. Numbering of the carbon chain should be done from that end which is nearer to the double bond:



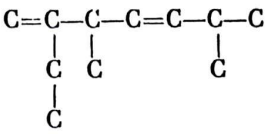
The position of the double bond (with numerals 1 and 2 above) is indicated by the lower of the two numerals on the carbon atoms forming the double bond. Therefore, the given alkene will be named as 4-methyl-1-pentene.

Example 2. Name the following alkene skeleton by the IUPAC nomenclature:

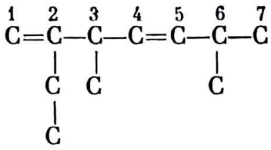


Solution. 3-Ethyl-5-methyl-2-hexene.

Example 3. Name the following unsaturated hydrocarbon containing two double bonds:

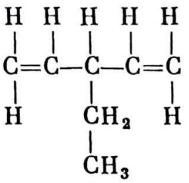


Solution. Let us number the carbon chain in such a way that the double bonds are denoted by the lowest numbers:



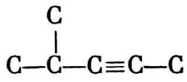
Now by arranging the substituents alphabetically, we get the name for the given hydrocarbon: 2-ethyl-3,6-dimethyl-1,4-heptadiene.

Example 4. Name the following compound and write the condensed structural formula for it:

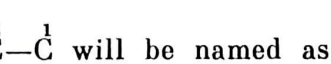


Solution. Name: 3-ethyl-1,4-pentadiene. Condensed formula: $CH_2=CHCH(C_2H_5)CH=CH_2$.

Example 5. Name the following alkyne and write its condensed structural formula:



Solution. Alkynes derive their names from the names of the corresponding alkanes by replacing the suffix 'ane' by 'yne'. The other rules remain the same. Hence



will be named as 4-methyl-2-pentyne. The condensed structural formula is $CH_3CH(CH_3)C{\equiv}{\equiv}CCH_3$.

Example 6. Calculate the mass percent of CaC_2 in technical-grade calcium carbide from the following data: a 1.6-g sample of it produced 0.38 litre of acetylene at 17 °C and 750 mm.

Solution. The equation for the reaction yielding acetylene is:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

The given volume of acetylene on conversion to STP will be

$$V_0 = \frac{pV273}{p_0(273 + t°C)} = \frac{750 \cdot 0.38 \cdot 273}{760 \cdot 290} = 0.353 \text{ litre}$$

Now the mass of calcium carbide in the technical-grade sample may be calculated as follows:

22.4 litres of C_2H_2 evolve from 64 g of CaC_2

0.353 litre of C_2H_2 evolves from $\frac{0.353 \text{ litre} \times 64 \text{ g}}{22.4 \text{ litres}}$

$= 1$ g of CaC

Next, 1.6 g of CaC_2 constitute 100%

$$1 \text{ g of } CaC_2 \text{ constitutes } \frac{1 \text{ g} \times 100\%}{1.6 \text{ g}} = 62.5\%$$

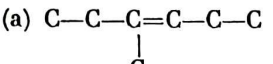
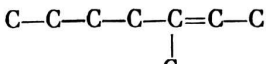
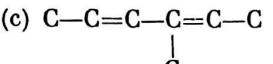
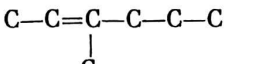
Therefore, the given technical-grade calcium carbide contains 62.5% by mass of CaC_2.

PROBLEMS AND EXERCISES

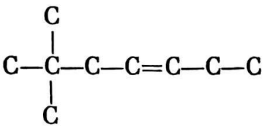
1. Which hydrocarbons are called unsaturated?
2. Characterize the nature of the double bond in unsaturated hydrocarbons.
3. Name the first five members of the homologous series of unsaturated hydrocarbons on the basis of the general formula.
4. Which of the following carbon skeletons represents 3-heptene?

(a) C—C—C=C—C—C—C (b) C—C—C=C—C—C
(c) C—C—C—C—C=C—C (d) C—C—C—C—C=C—C—C

5. Amongst the following carbon skeletons which one depicts 3-methyl-2-hexene?

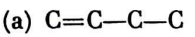
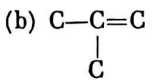
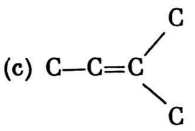
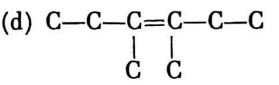
(a) 
(b) 
(c) 
(d) 

6. Which name is correct for the alkene with the following carbon skeleton:

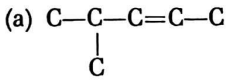
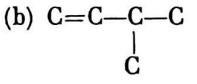
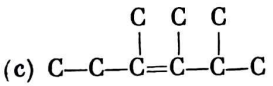
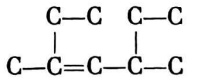


(a) 2-dimethyl-3-heptene
(b) 6,6-dimethyl-3-heptene
(c) 6,6-dimethyl-4-heptene
(d) 2,2-dimethyl-4-heptene

7. Give the rational names for the alkenes, the carbon skeletons of which are shown below:

(a) 
(b) 
(c) 
(d) 

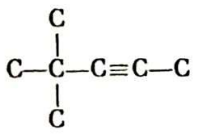
8. Name the unsaturated hydrocarbons shown below by the carbon skeletons by the systematic nomenclature

(a) 
(b) 
(c) 
(d) 

9. Which of the following condensed structural formulas corresponds to 3-methyl-2,4-hexadiene?

(a) $CH_3C(CH_3)=CHCH=CHCH_3$
(b) $CH_3CH=CH(CH_3)CH=CHCH_3$
(c) $CH_2=C(CH_3)CH=CHCH_2CH_3$
(d) $CH_3CH=C(CH_3)CH_2CH=CH_2$

10. Of the names listed below choose the one corresponding to the following carbon skeleton:



(a) 2,2-dimethyl-3-pentyne
(b) 4,4-dimethyl-2-pentyne
(c) 2-dimethyl-4-pentyne
(d) 4,4-dimethyl-3-pentyne

11. What are polymerization reactions? What are the conditions under which these reactions occur?

12. What are the characteristic features of a triple bond? How does it differ from a double bond?

13. Write the structural formulas for (a) ethylethylene, (b) propylethylene, (c) *symm*-dimethylethylene, (d) *nonsymm*-methylethylethylene, (e) *nonsymm*-methylisopropylethylene, (f) *symm*-diisopropylethylene.

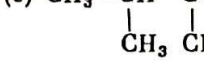
14. Write the structural formulas for (a) α,β-methylethylethylene, (b) α,β-ethylisopropylethylene, (c) α,α-methylethylethylene, (d) α,α-methylisobutylethylene.

15. Write the structural formulas for (a) 2-methyl-2-butene, (b) 2-methyl-1-propene, (c) 2,3-dimethyl-3-hexene, (d) 2,5,5-trimethyl-2-hexene, (e) 4-ethyl-2,2,6-trimethyl-3-heptene.

16. Name the following unsaturated hydrocarbons according to the rational nomenclature:

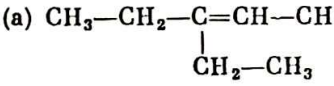
(a) $CH_3-CH=CH-CH_2-CH_3$

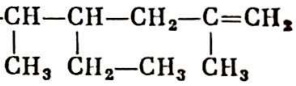
(b) $CH_3-CH_2-CH=CH-CH_2-CH_3$

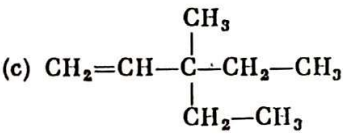
(c) 

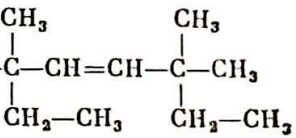
(d)

17. Give the IUPAC names for the following alkenes:

(a) 

(b) 

(c) 

(d) 

18. Write the structural formulas for (a) 2-methyl-1,3-butadiene, (b) 2-methyl-1,5-hexadiene, (c) 2,4-dimethyl-2,4-pentadiene, (d) 2-methyl-1,3-pentadiene.

19. Give the IUPAC names for the following alkadienes:

(a) $CH_2=CH-CH=CH-CH_3$

(b) $CH_2=CH-\underset{\displaystyle CH_3-CH_2}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2$

(c) $CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$

(d) $CH_3-CH=\underset{\displaystyle CH_3-H_2C}{\underset{|}{C}}-\underset{\displaystyle CH_2-CH_3}{\underset{|}{C}}=CH-\underset{\displaystyle CH_3}{\underset{\diagdown}{CH}}-CH_3$

20. Which olefins can be prepared when the following compounds are dehydrogenated: (a) isobutane, (b) dimethylethylmethane, (c) 2-methylpentane, (d) propane? Write the condensed structural formulas both for the reactants and products.

21. Which hydrocarbons and in what amounts are obtained on dehydration of 10 kg of (a) ethyl alcohol, CH_3-CH_2-OH; (b) propyl alcohol, $CH_3-CH_2-CH_2-OH$?

22. How much and which hydrocarbons are obtained by reacting 500 ml of an alcoholic sodium hydroxide solution having a density of 0.7 g/ml and containing 40 mass percent of NaOH with the following halogen derivatives: (a) 1-chloropropane, (b) 2-chlorobutane?

23. How many grams of bromine can react with (a) 2.8 g of 2-butene, (b) 3.5 g of α,β-methylethylethylene, (c) 4.2 g of *nonsymm*-methylpropylethylene?

24. What volume of hydrogen is required to hydrogenate 12.4 g of a gas mixture containing 22.58% ethylene, 32.26% propene and 45.16% 2-butene (by mass)? Write the equations for the involved reactions.

25. 2.5 litres of a mixture of ethane and ethylene are passed through an aqueous solution of bromine. As a result, 4.7 g of ethylene dibromide are formed. Determine the volume percents of ethane and ethylene in the mixture.

26. Carbon dioxide prepared by burning 8.4 litres of ethylene (STP) was absorbed by 472 ml of a sodium hydroxide solution (density 1.06 g/ml) containing 6% by mass of NaOH. What is the composition of the produced salt? What is its percent strength?

27. Write the equations for the reactions involved in the following conversions:

$$C \rightarrow CH_4 \rightarrow CH_3Cl \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_5OH$$

28. How many grams of a haloderivative are produced when 1.12 litres of propylene are reacted with hydrogen chloride? Represent the involved reaction using structural formulas taking into account the Markownikoff rule.

29. What is the volume of hydrogen liberated after dehydrogenation of 500 m^3 of *n*-butane, if the volume of the obtained 1,3-butadiene is 400 m^3?

30. How many litres of divinyl are formed from 2 litres of 95% C_2H_5OH solution (density 0.79 g/ml)? The yield of divinyl is 90% of the theoretical amount calculated on the basis of the employed raw materials.

31. Write the structural formulas for (a) diethylacetylene, (b) methylisopropylacetylene, (c) propylisopropylacetylene and (d) ethylpropylacetylene.

32. Write the structural formulas for (a) 1-butyne, (b) 2-pentyne, (c) 4,4-dimethyl-2-pentyne, and (d) 2,2,5-trimethyl-3-hexyne.

33. Name the following hydrocarbons according to the IUPAC nomenclature:

(a) $CH_3-C\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$

(c) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-C\equiv C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$

(d) $CH_3-\underset{\displaystyle CH_2-CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH-C\equiv C-CH_3$

34. Determine the mass of calcium carbide obtained when 28 kg of calcium oxide are fused with 30 kg of carbon.

35. 120 kg of technical-grade calcium carbide were treated with water to liberate 33.6 m^3 of a gas measured at STP. Determine the mass percent of pure calcium carbide in the technical-grade sample.

36*. Acetylene prepared from technical-grade calcium carbide containing 7% by mass of impurities was passed

through an excess solution of bromine in carbon tetrachloride to yield 34.6 g of a bromide. How many grams of the technical-grade calcium carbide were used for this reaction? How many litres of acetylene were formed at standard conditions?

37. Calculate the mass percent of calcium hydroxide solution obtained by treating 32 g of calcium carbide with 200 ml of water.

38. How many grams of acetaldehyde may be prepared from 50 litres of acetylene by the Kucherov method, if it is known that the yield of the aldehyde is 90% of the theoretical amount?

39. What volume of acetylene is required to prepare 40 kg of benzene?

40. How many grams of vinyl chloride will be produced when 30 litres of acetylene react with 20 litres of hydrogen chloride? Determine the mass percent of the gas that entered into the reaction.

41. What volume of hydrogen is required to hydrogenate 10 litres of a mixture containing 20% ethene and 80% ethyne (by mass)? What is the volume of ethane thus produced?

42. How many litres of air will be needed for complete combustion of 50 litres of a mixture containing 60% ethylene and 40% acetylene (by mass)?

43*. A volume of 34.25 ml of 44.8% KOH solution (density 1.46 g/ml) was required to absorb carbon dioxide produced when 6.72 litres of a mixture of methane and acetylene were burnt. Determine the mass percents of the components in the initial mixture and calculate the concentration of the solution formed after carbon dioxide had been absorbed, if it is known that an acid salt was produced as a result of the reaction.

44*. A mass of 4 g of a precipitate was formed when carbon dioxide produced during complete combustion of 336 ml of a mixture of propylene and acetylene measured at STP was passed into lime water. Determine the composition of the initial mixture of hydrocarbons in volume percents.

45. How many litres of oxygen measured at STP will be required for complete combustion of 6.5 g of acetylene? What mass of an aqueous caustic soda solution containing

25% by mass of NaOH was used for absorbing the produced carbon dioxide, if this yielded a neutral salt?

46. How many litres of air and oxygen, respectively, will be required for complete combustion of 13 kg of acetylene?

47. A mass of 8 g of hydrogen was formed when an ammonia solution of silver oxide was treated with acetylene. Calculate the amount of acetylene used (in litres) and the mass of the isolated silver acetylide.

48. How many litres of oxygen measured at STP are required for burning 1 mole of propylene?

49. Calculate the number of propane molecules per propylene molecule in a mixture from the following data: 8.6 g of the mixture of propane and propylene absorb 16 g of bromine.

50. Calculate the volume of ethane which may be produced from 100 m^3 of ethylene at STP by saturating the latter with hydrogen.

51. How many litres of ethane will be formed at STP when 39 g of acetylene react with 50 litres of hydrogen?

52. Determine the volume of hydrogen chloride at STP and the mass of carbon black formed when 130 g of acetylene are burnt in chlorine.

53. Air containing 2.5 to 8.3 mass percent of acetylene as an impurity explodes on heating. Calculate the volume of acetylene in one litre of air that may cause an explosion.

54. How many grams of bromine may react with 1.12 litres of ethylene at standard conditions?

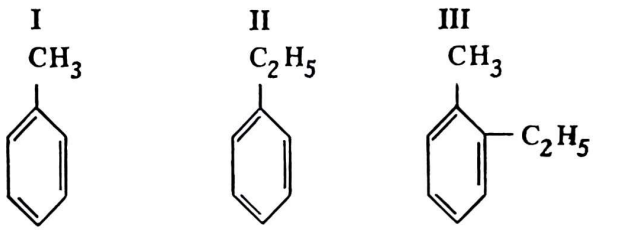
55. Combustion of 4.48 litres of a gas yielded 13.44 litres of carbon dioxide and 10.8 g of water. The mass of one litre of this gas equals 1.875 g at STP. Derive the true (molecular) formula of the gas.

56. Determine the volumes of ethylene and chlorine at standard conditions required to produce 19.8 g of dichloroethane.

57. 40 litres of ethylene measured at STP are obtained by passing 92 g of ethyl alcohol over heated aluminium oxide. Calculate the percent yield of ethylene relative to the theoretically possible amount.

6.3 AROMATIC HYDROCARBONS

The term "aromatic compounds" became known in the second half of the 19th century. In those days compounds isolated from natural resins and essential oils that had pleasant smell were called aromatic compounds. But now this name has nothing to do with odour, because numerous benzene derivatives have been produced which are either odourless, or have unpleasant smell. It has been established that the basis of these hydrocarbons is the nucleus of the hydrocarbon benzene, C_6H_6. This is why all compounds which are derivatives of benzene came to be known as the aromatic compounds. They are derived by replacing one or more hydrogen atoms in the benzene ring by other atoms or groups of atoms. In the rational nomenclature, the names of hydrocarbons of the benzene series are formed from the names of the radicals or groups in the side chains by adding the suffix "benzene":



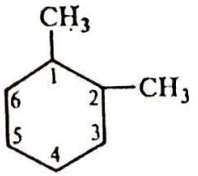
methylbenzene ethylbenzene methylethylbenzene

On the other hand, these very hydrocarbons may be considered as the derivatives of an aliphatic hydrocarbon in which one hydrogen atom has been replaced by a monovalent benzene radical, $-C_6H_5$, called phenyl. In this case hydrocarbons I and II are named as phenylmethane and phenylethane, respectively.

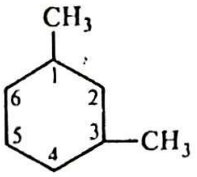
Several benzene homologues have empirical (trivial) names. For example, methylbenzene, $C_6H_5CH_3$, is known as toluene, dimethylbenzene, $C_6H_4(CH_3)_2$, is called xylene, and so on.

If a benzene ring contains one substituent, no isomerism is possible, since all carbon atoms in benzene are equivalent. Depending upon how two or more substituents

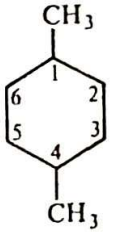
are arranged with respect to one another, aromatic compounds can have different isomers. To take one example, dimethyl benzene, $C_6H_4(CH_3)_2$, or xylene may exist in the form of three isomers. To specify the positions of the substituents in a benzene ring, the carbon atoms are numbered as shown below:



1,2-dimethylbenzene



1,3-dimethylbenzene



1,4-dimethylbenzene

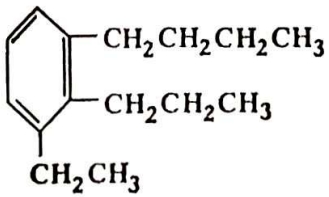
In addition to the numerical designations, other types of designations for the substituents are also used.

1. If the substituents are attached to the neighbouring carbon atoms, such isomers are called *ortho*-isomers. 1,2-Dimethylbenzene is, therefore, named as *ortho*-dimethylbenzene, or *o*-dimethylbenzene.

2. If the two substituents are attached to the carbon atoms that are separated by one carbon atom, then the isomers with such an arrangement of substituents are called *meta*-isomers. 1,3-Dimethylbenzene is, therefore, named as *meta*-dimethylbenzene, or *m*-dimethylbenzene.

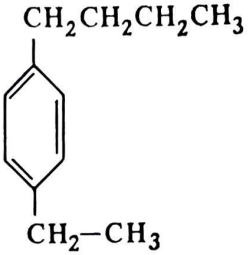
3. If the two substituents are attached to the carbon atoms that are separated by two carbon atoms, such isomers are *para*-isomers. Hence, 1,4-dimethylbenzene should be named as *para*-dimethylbenzene or *p*-dimethylbenzene.

Example 1. Name the following derivative of benzene:



Solution. 1-Butyl-3-ethyl-2-propylbenzene (the names of the groups are arranged in alphabetical order).

Example 2. Among the systematic names given below which one is correct for the given aromatic hydrocarbon?

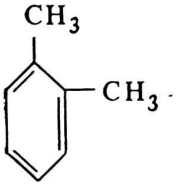


(a) 4-butyl-1-ethylbenzene, (b) 1-ethyl-4-butylbenzene, (c) 1-butyl-4-ethylbenzene.

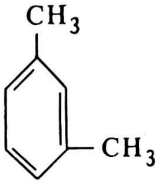
Solution. 1-Butyl-4-ethylbenzene.

Example 3. What are the possible structures for the aromatic hydrocarbon with a molecular formula of C_8H_{10}? Name the possible isomers according to the systematic nomenclature and according to the IUPAC rules.

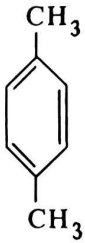
Solution. The aromatic compound C_8H_{10} has four possible isomers:



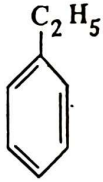
1,2-dimethylbenzene (*ortho*-dimethylbenzene)



1,3-dimethylbenzene (*meta*-dimethylbenzene)



1,4-dimethylbenzene (*para*-dimethylbenzene)



ethylbenzene

PROBLEMS AND EXERCISES

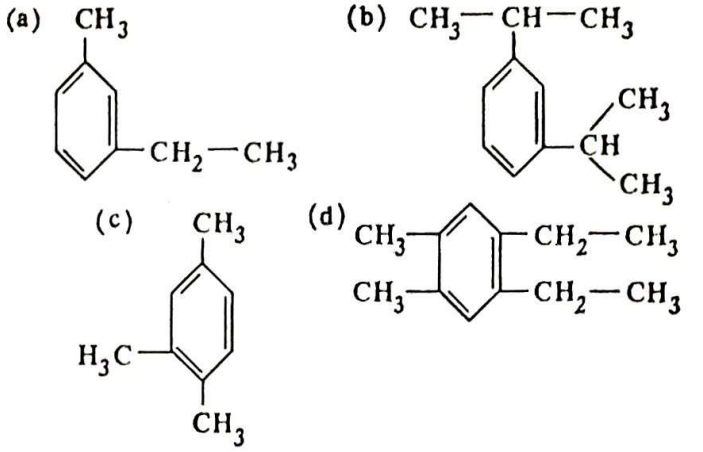
1. Which hydrocarbons refer to aromatic compounds?
2. What are the contradictions between the structural formula suggested by Kekule and the properties of benzene?

3. How will you explain the structure of benzene from the viewpoint of the electron delocalization theory?

4. How many isomers are possible for triethylbenzene?

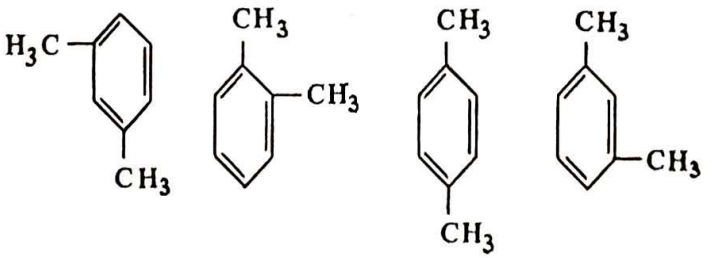
5. Do the following compounds have isomers: (a) bromohexane, (b) bromobenzene, (c) cyclohexyl bromide?

6. Name the following compounds:

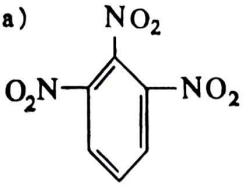


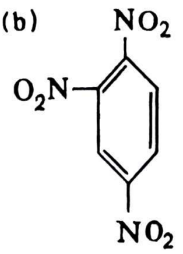
7. Of the three ordinary names given below which one is correct for 1,3-dimethylbenzene
(a) *ortho*-xylene (b) *para*-xylene (c) *meta*-xylene?

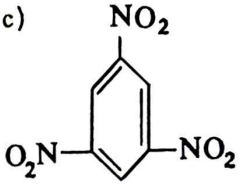
8. How many substances are represented below?



9. Which of the following formulas belongs to 1,3,5-trinitrobenzene?

(a) 

(b) 

(c) 

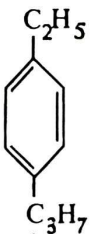
10. What are the similarities and what are the differences between saturated and unsaturated hydrocarbons?

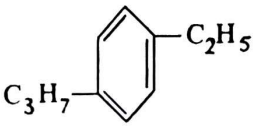
11. Write the structural formulas for 3-ethyl-2-methylbenzene, 1,3,5-trimethylbenzene, 4-isobutyl-1-methylbenzene and 1,4-diisopropylbenzene.

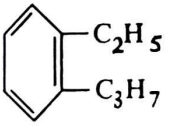
12. Write the structural formulas for *o*-ethylmethylbenzene, *p*-diethylbenzene and *m*-methylisopropylbenzene.

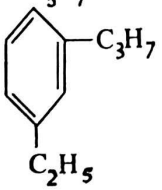
13. Write the structural formulas for phenylpropane, phenylhexane, phenylethane and phenylbutane.

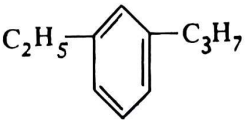
14. How many compounds are depicted below? Name them.

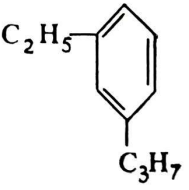
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

15. How may benzene be prepared from methane? How many litres of methane are required in order to prepare 7.8 g of benzene?

16. How much benzene may be prepared from 10 m^3 of acetylene? The yield of benzene is 30% of the theoretical amount.

17. How many grams of toluene will be produced by reacting 15.6 g of benzene with chloromethane?

18. Write down the reaction equations for (a) bromination, (b) nitration, and (c) sulphonation of benzene to yield monosubstituted benzene derivatives. Also name the products thus formed.

19. What volume of 90% HNO_3 solution (density 1.483 g/ml) will be required for the nitration of benzene to yield 24.6 g of nitrobenzene?

20. How many grams of benzene sulphonic acid will be produced by reacting benzene with 200 ml of a sulphuric acid solution of density 1.83 g/ml which contains 94% by mass of H_2SO_4?

21. Calculate the mass of monobromobenzene which will be produced when 100 kg of benzene are brominated, the yield of the product being 40%.

22. What volume of hydrogen will be required in order to hydrogenate 20 kg of benzene to cyclohexane in the presence of a catalyst?

23. How many grams of hexachlorocyclohexane may be prepared from 15.6 g of benzene and 15 litres of chlorine by exposing to irradiation?

24. Calculate the mass of benzene that may be obtained from 201.6 litres of acetylene at standard conditions.

25. Calculate the vapour density for benzene with respect to (a) air and (b) hydrogen.

26. Calculate the volume of air required for burning 117 g of benzene.

27. How many grams of bromobenzene may be prepared when 117 g of benzene are brominated with 316 g of bromine? Which of the initial substances is taken in an excess amount?

28. What volume of acetylene at STP is needed in order to prepare 886 ml of benzene of density 0.88 g/ml? The yield of benzene is 75% of the theoretical amount.

29. A mass of 30 g of bromobenzene was produced when 15.6 g of benzene were treated with an excess bromine. Calculate the yield of bromobenzene in mass percent of the theoretical amount.

30. What volume of hydrogen measured at standard conditions will add to 234 g of benzene to hydrogenate the latter to cyclohexane?

31. How many grams of bromobenzene may be prepared from 1.5 litres of benzene of density 0.88 g/ml?

32. How many grams of toluene will be required to prepare 113.5 g of trinitrotoluene, if the yield of the product is 82% of the theoretical amount.

33. Combustion of 31.2 g of an organic compound, whose vapour density with respect to air is 2.69, yielded 53.76 litres of carbon dioxide and 21.6 g of water. What is the structural formula of this compound?

34. Calculate the mass of cyclohexane and the volume of chlorine required to prepare 1 kg of hexachloran.

7
ORGANIC COMPOUNDS CONTAINING OXYGEN

7.1 ALCOHOLS AND PHENOLS

Alcohols are the derivatives of hydrocarbons in which one or more hydrogen atoms are replaced by hydroxyl group(s).

Depending on the number of hydroxyl groups, alcohols are classified as (a) monohydric, containing one hydroxyl group and (b) polyhydric, having two, three and more hydroxyl groups.

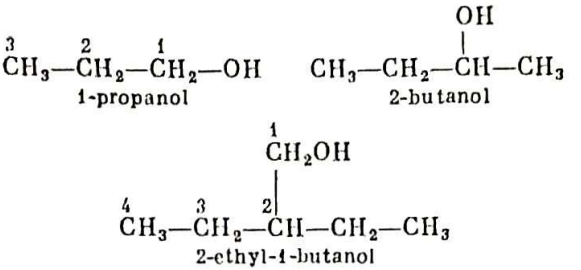
The monohydric alcohols of the alkane series form a homologous series in which the neighbouring members differ by a $-CH_2-$ group (methylene group). The general formula for such alcohols is $C_nH_{2n+1}OH$.

According to the rational nomenclature, alcohols of the alkane series are named by adding the word "alcohol" to the relevant radical or group:

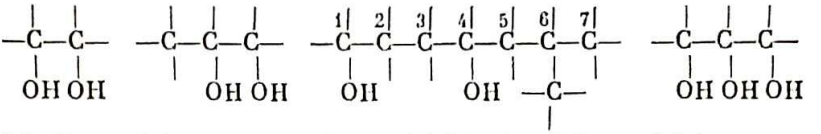
CH_3OH	CH_3-CH_2-OH	$CH_3-CHOH-CH_3$
methyl alcohol	ethyl alcohol	isopropyl alcohol

According to the IUPAC rules, the names of alcohols are derived from those of hydrocarbons by replacing 'e' by 'ol'. Besides this, a numerical prefix is used to indicate the position of the hydroxyl group on the carbon chain. Since OH is the functional group, the largest carbon chain involving this group is selected as the parent chain and the numbering is done in such a way that the carbon with the OH group gets the lowest possible number. Here

are a few examples:

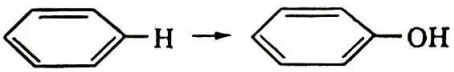


There are alcohols that contain two and three hydroxyl groups. In the IUPAC system, they are named by adding the suffixes 'diol' (for dihydric) and 'triol' (for trihydric) to the name of the respective hydrocarbon:

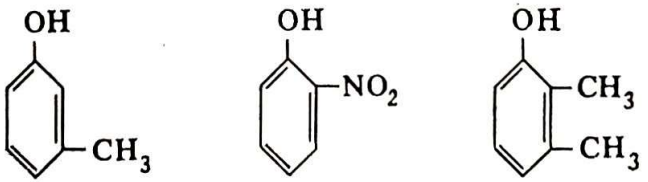


1,2-ethanediol (ethylene glycol) | 1,2-propanediol | 6-methyl-1,4-heptanediol | 1,2,3-propanetriol (glycerol)

The simplest aromatic hydroxy compound, C_6H_5OH, has the trivial name *phenol*. It is a hydrocarbon derivative which may be considered as a product of replacement of a hydrogen atom in the nucleus of an aromatic hydrocarbon by the hydroxyl group:

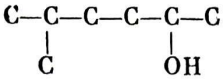


Derivatives of phenol are known as substituted phenols. For example:



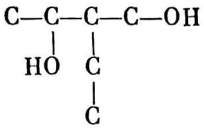
3-methylphenol | 2-nitrophenol | 2,3-dimethylphenol

Example 1. Name the following monohydric alcohol



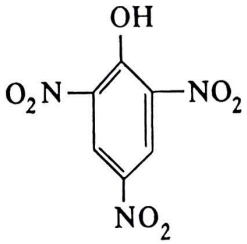
Solution. While choosing the proper numbering, a functional group is always preferred to other substituents. Hence the given alcohol will be named as 5-methyl-2-hexanol.

Example 2. Name the dihydric alcohol presented below:

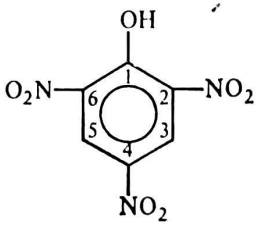


Solution. 2-Ethyl-1,3-butanediol.

Example 3. Name the following derivative of phenol according to the IUPAC nomenclature:



Solution. The IUPAC name is 2,4,6-trinitrophenol. The formula exhibiting numbering is as follows:



Example 4. An excess sodium was placed in 16.6 g of a mixture of ethanol and propanol. As a result, 3.36 litres of hydrogen measured at STP were liberated. What is the composition of the original mixture of alcohols?

Solution. Let X g be the mass of ethanol and $(16.6 - X)$ g be the mass of propanol.

1. The volume of hydrogen liberated by the action of sodium on ethanol:

$$2C_2H_5OH + 2Na = 2C_2H_5ONa + H_2$$

2×46 g of ethanol yield 22.4 litres of H_2

X g of ethanol yields $\frac{22.4X}{2 \times 46}$ litres of H_2

2. The volume of hydrogen evolved when sodium acts on propanol:

$$2C_3H_7OH + 2Na \rightarrow 2C_3H_7ONa + H_2$$

2×60 g of propanol yield 22.4 litres of H_2

$(16.6 - X)$ g of propanol yield $\frac{(16.6 - X) \times 22.4}{2 \times 60}$ litres of H_2

3. Since the total volume is 3.36 litres, we can write:

$$\frac{22.4X}{2 \times 46} + \frac{(16.6 - X) \times 22.4}{2 \times 60} = 3.36 \text{ whence } X = 4.6 \text{ g}$$

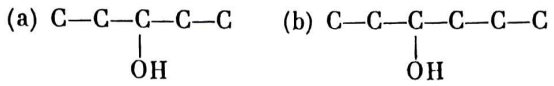
The given mixture, therefore, contains 4.6 g of C_2H_5OH and $16.6 - 4.6 = 12$ g of C_3H_7OH.

PROBLEMS AND EXERCISES

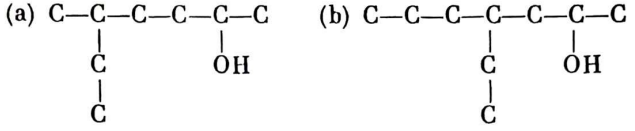
1. Which compounds belong to alcohols? How are they classified?
2. What are the three industrial methods of preparation of ethyl alcohol that you know? Which method is the most economic?
3. How can you obtain diethyl ether and ethylene from ethyl alcohol?
4. Which products are formed when methyl and ethyl alcohols are oxidized?
5. How can you prove the mobility of the hydroxyl group in monohydric alcohols?
6. What are the chemical properties of the following compounds:

(a) $CH_3-CH=CH-CH_2OH$ (b) $CH_3-CH_2-CH_2-CH_2OH$

7. Which of the following skeleton formulas depicts 3-pentanol:



8. Which of the following skeleton formulas corresponds to 5-methyl-2-heptanol:



9. What is produced when alcohols are dehydrogenated?

10. Write down the reaction equations for preparing propyl and isopropyl alcohols.

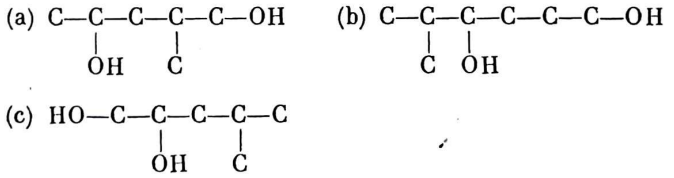
11. Which qualitative reaction can be used to distinguish between monohydric and polyhydric alcohols?

12. How will you prepare ethylene glycol from ethyl alcohol?

13. Which ether is formed when a mixture of methyl alcohol and concentrated sulphuric acid is heated?

14. State whether the simplest dihydric alcohol, methylene glycol, exists or not.

15. Which of the skeleton formulas displayed below describes 2-methyl-1,4-pentanediol:



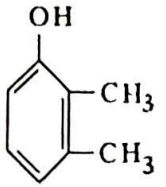
16. What is nitroglycerine and what class of compounds does it belong to?

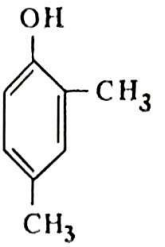
17. Where are 1,2-ethanediol and 1,2,3-propanetriol used?

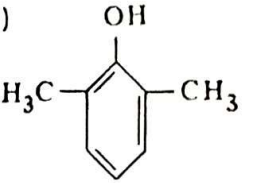
18. What is the composition and the structural formula of phenol?

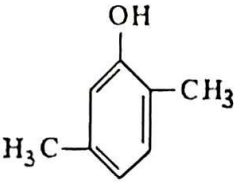
19. What are the main methods for phenol preparation?

20. Indicate the structural formula which corresponds to 2,4-dimethylphenol:

(a) 

(b) 

(c) 

(d) 

21. Write the equations for reactions that are characteristic of phenols and monohydric alcohols.

22. With which substances does phenol (a) form a white precipitate, (b) give a violet colouration, (c) turn pink?

23. Where is phenol used?

24. Write the structural formulas for the isomers of butyl alcohol and name them according to the rational and IUPAC nomenclatures.

25. Give the rational names for the following alcohols:

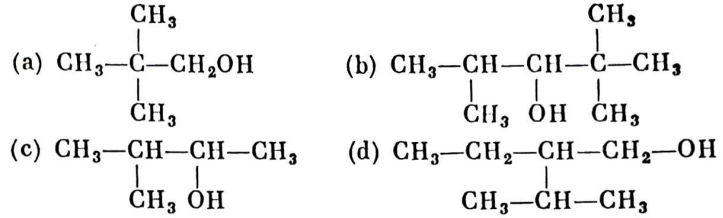
(a) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$ (b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-OH$

(c) $CH_3-CH_2-CH_2-OH$

(d) $CH_3-CH_2-CH_2-CH_2-CH_2-OH$

26. Write down the structural formulas for the following monohydric alcohols: (a) 2-methyl-2-propanol, (b) 2,3-dimethyl-3-pentanol, (c) 2,4,4-trimethyl-2-pentanol, and (d) 2,3-dimethyl-2-butanol.

27. Name the alcohols displayed below according to the IUPAC nomenclature:



28. Write the equations for reactions that can be used to carry out the following conversions:

(a) $CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_5OH \rightarrow C_2H_5ONa$

(b) $CaC_2 \rightarrow C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6 \rightarrow C_2H_5Cl \rightarrow C_2H_5OH$

29. How many tons of alcohol that would contain 96% by mass of C_2H_5OH may be prepared by direct hydration of 1 ton of ethylene?

30. How many kilograms of propyl alcohol are formed when 15.7 kg of propyl iodide are hydrated?

31. Determine the mass percents of components produced when 150 ml of an ethanol solution having a density of 0.8 g/ml and containing 95% by mass of C_2H_5OH react with 46 g of sodium, taking into account that the whole of water present in the given alcohol solution reacts with sodium.

32*. How many litres of ethylene are formed when a mixture of an excess concentrated sulphuric acid and 200 ml of 96% C_2H_5OH solution (density 0.8 g/ml) is heated at 160 °C? How many millilitres of diethyl ether (density 0.7 g/ml) may be obtained from the same amount of alcohol by heating the mixture at 140 °C when the acid is in shortage?

33. When 46.25 g of a monohydric alcohol were heated with concentrated sulphuric acid, 11.2 litres of an unsaturated hydrocarbon with one double bond were formed. Derive the formula of the alcohol, if 80% of the whole alcohol entered into the dehydration reaction. Write the structural formulas for the isomers of this alcohol and name them according to the IUPAC nomenclature.

34. 30 g of an alcohol are heated with sulphuric acid to yield 3.92 litres of a gaseous hydrocarbon containing

one double bond. The yield of the produced hydrocarbon is 35%. What is the structure of the original alcohol?

35. How many grams of ethyl bromide will be produced when ethyl alcohol is heated with 120 ml of a hydrobromic acid solution of density 1.2 g/ml, which contains 40% by mass of HBr?

36. How many grams of acetaldehyde may be prepared by dehydrogenation of 100 ml of 95.5% C_2H_5OH solution (density 0.79 g/ml)? The yield of the aldehyde is 90% of the theoretical amount.

37. What volume of air containing 21% oxygen is required for burning 500 ml of ethyl alcohol having a density of 0.8 g/ml and containing 96 mass percent of C_2H_5OH? How many litres of carbon dioxide will be liberated as a result of this reaction?

38*. 1.24 g of a mixture of methyl and ethyl alcohols in 50 ml of benzene of density 0.88 g/ml were treated with an excess metallic sodium to evolve 336 ml of a gas at STP. Determine the mass percent of each alcohol in the solution.

39*. Complete combustion of 1.74 g of a mixture of methyl and ethyl alcohols requires 2016 ml of oxygen at STP. Determine the mass percents of the alcohols in the original mixture.

40. What volume will occupy an ethylene glycol solution having a density of 1.2 g/ml and containing 60% by mass of $HOCH_2CH_2OH$ obtained as a result of hydrolysis of 33 g of dichloroethane?

41. How much 1,2-ethanediol can be prepared from 250 kg of ethylene oxide and 90 kg of water? Which of the two starting materials has been taken in excess amount and what is its percent?

42*. How much 1,2-ethanediol is obtained when ethylene is oxidized with atomic oxygen evolved from 15.8 g of potassium permanganate?

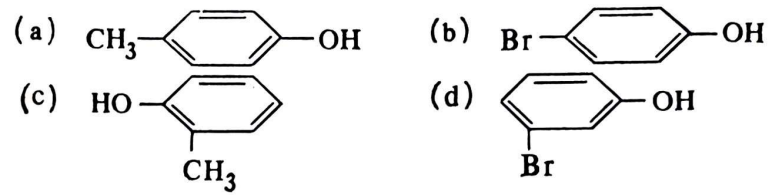
43. What volume of hydrogen will be given off when 4 g of ethylene glycol react with 2.3 g of metallic sodium?

44. Cupric hydroxide is prepared by reacting 14 ml of a sodium hydroxide solution having a density of 1.42 g/ml and containing 40 mass percent of NaOH with cupric sulphate. What mass percent of this cupric hydrox-

ide will be required to form (a) 6.2 g of copper glycolate, (b) 3.45 g of copper glycerate?

45. How many millilitres of 80% HNO_3 solution (density 1.45 g/ml) will be required in order to prepare 22.7 g of glyceryl trinitrate?

46. Name the following compounds:



47. Write the reaction equations for the following conversions:

$$CH_4 \rightarrow C_2H_2 \rightarrow C_6H_6 \rightarrow C_6H_5Cl \rightarrow C_6H_5OH$$

48. Write the reaction equations and specify the conditions for preparing phenol from (a) benzene sulphonic acid, (b) bromobenzene, (c) coal tar.

49. How many kilograms of phenol may be prepared from 10 kg of potassium phenolate? How many litres of a sulphuric acid solution of density 1.8 g/ml which contains 90% by mass of H_2SO_4 will be used for this purpose?

50. What mass of chlorobenzene will be needed to produce 4.7 g of phenol?

51. Determine the mass percents of the components which are obtained by reacting 9.4 g of phenol with 7 ml of a sodium hydroxide solution having a density of 1.43 g/ml and containing 40 mass percent of NaOH.

52. 150 ml of 2 *M* potassium hydroxide solution were required to completely neutralize 21.4 g of a solution of phenol in acetic acid. Determine the percent strength of the original solution.

53. A mass of 4.97 g of tribromophenol was obtained when phenol was treated with bromine water. How many grams of phenol were used for this reaction?

54. How many millilitres of 68% HNO_3 solution (density 1.4 g/ml) will enter into reaction with phenol to yield 22.9 g of 2,4,6-trinitrophenol?

55. A mixture of ethyl alcohol and phenol yielded 2.24 litres of hydrogen, when treated with metallic

sodium, and 33.1 g of tribromophenol, when treated with bromine. Determine the mass percents of the components in the original mixture.

56. 25 ml of a potassium hydroxide solution having a density of 1.4 g/ml and containing 40% by mass of KOH were required to neutralize 100 g of an aqueous solution of phenol. How many grams of an aqueous bromine solution containing 1% by mass of bromine should be added to the phenol solution in order to precipitate the whole of phenol?

57. What volume will occupy hydrogen obtained by the action of 3.45 g of sodium upon 46 g of ethyl alcohol?

58. 1.7 kg of ethanol are obtained from 20 kg of ethylene during one cycle in a contact chamber. What percent of the theoretical yield does this constitute?

59. What volume of ethylene will be needed at standard conditions for the reaction with 7.2 g of water, if it is known that the yield of ethanol is 85% of the theoretical amount?

60. When 3.45 g of an organic compound consisting of hydrogen, carbon and oxygen were burnt, 6.6 g of carbon dioxide and 4.05 g of water were formed. The compound has a vapour density of 1.59 with respect to air. Determine the molecular formula of the compound and write the structural formulas for its isomers.

61. 0.32 g of a saturated monohydric alcohol reacts with metallic sodium to liberate 112 ml of hydrogen. What is the structural formula of the alcohol?

62. Will a mass of 69 g of sodium suffice to completely replace hydrogen in the hydroxyl groups of glycerine of density 1.26 g/ml, if 72.7 ml of the glycerine have been used for the reaction?

63. How many grams of potassium phenolate can be prepared from potassium hydroxide and phenol each weighing 20 g?

64. How many kilograms of phenol will be produced from 78 kg of benzene, if the production loss is 15%?

65. How many grams of a product will be produced by mixing 25 g of 95% C_6H_5OH solution with 80 g of an aqueous bromine solution which contains 1% by mass of bromine?

66. 85 g of ethanol are obtained from 129 g of chloroethane. What is the percent yield of ethanol relative to the theoretical amount?

7.2 ALDEHYDES

Aldehydes are organic compounds the molecules of which contain a carbonyl group, $-\overset{\overset{O}{\parallel}}{C}-H$, attached to an alkyl or aryl radical.

The general formula for the aldehydes is $R-\overset{\overset{O}{\parallel}}{C}-H$. The rational names for the members of the homologous series of aldehydes follow from the names of saturated acids obtained by oxidation of these aldehydes.

In the IUPAC nomenclature of the aldehydes, the class suffix is 'al'. The carbon of the carbonyl group is regarded as the first in the chain of carbon atoms. The longest chain including the —CHO group is selected as the parent hydrocarbon and the aldehyde is named by replacing the 'e' of the corresponding alkane by 'al'.

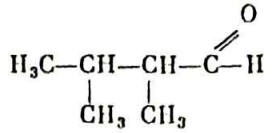
The rational (trivial) and IUPAC names of the first four members of aldehyde series are given in Table 7.1.

Table 7.1 Names of Aldehydes

Molecular formula	Trivial (rational) name	IUPAC name
$H-\overset{\overset{O}{\parallel}}{C}-H$	Formaldehyde	Methanal
$CH_3-\overset{\overset{O}{\parallel}}{C}-H$	Acetaldehyde	Ethanal
$CH_3-CH_2-\overset{\overset{O}{\parallel}}{C}-H$	Propionaldehyde (propionic aldehyde)	Propanal
$CH_3-CH_2-CH_2-\overset{\overset{O}{\parallel}}{C}-H$	*n*-Butyraldehyde	Butanal

Example 1. What is the structural formula of 2,3-dimethylbutanal? Write the condensed linear structural formula for this aldehyde.

Solution. The structural formula is as follows (the carbon atom of the carbonyl group always gets number 1):



The condensed linear formula is $CH_3CH(CH_3)CH(CH_3) \times CHO$.

Example 2. Determine the mass of calcium carbide that would contain 87% by mass of CaC_2 required to prepare 1 ton of glacial acetic acid, if the yield of the latter is 100%.

Solution. The main steps involved in the production of glacial acetic acid are as follows:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + HC{\equiv}CH$$

$$HC{\equiv}CH + H_2O \xrightarrow{Hg^{2+}} CH_3{-}\overset{\overset{O}{\|}}{C}{-}H$$

$$CH_3CHO \xrightarrow{[O]} CH_3COOH$$

From these equations it follows that from 1 mole (64 g) of CaC_2 one can prepare 1 mole (i.e. 60 g) of acetic acid. So we can calculate the amount of CaC_2 required to prepare 1 ton of acetic acid in the following way:

60 g of CH_3COOH are produced from 64 g of CaC_2

1 ton of CH_3COOH is produced from $\dfrac{1 \text{ ton} \times 64 \text{ g}}{60 \text{ g}}$

$= 1.067$ tons of CaC_2

Let X be the required mass of CaC_2 in ton. Now since the technical-grade calcium carbide contains 87% CaC_2, we can form the following relationship:

$1.067 : X = 87 : 100$, whence $X = 1.226$ tons

Example 3. A mass of 1347.39 kg of calcium carbide containing 95% by mass of the pure carbide was treated with water to yield a gas which was passed into a sulphuric

acid solution containing mercuric sulphate. The liquid thus obtained was reduced with hydrogen in the presence of nickel to produce a third product with a yield of 80% of the theoretical amount. Calculate the mass of the final product, assuming that it contains 95% pure compound and 5% water.

Solution. Let us first calculate the amount of pure calcium carbide in 1347.39 kg of the given impure calcium carbide:

100% constitute 1347.39 kg of CaC_2

95% constitute $95\% \times 1347.39$ kg/100% = 1280 kg of CaC_2

Now we can calculate the mass of alcohol produced from 1280 kg of pure CaC_2 as follows:

$$CaC_2 + 2H_2O \rightarrow \underset{\text{acetylene}}{C_2H_2} + Ca(OH)_2$$

$$C_2H_2 + H_2O \xrightarrow{H_2SO_4 + Hg^{2+}} \underset{\text{acetaldehyde}}{CH_3-C(=O)-H}$$

$$CH_3-C(=O)-H + H_2 \xrightarrow{Ni} \underset{\text{ethyl alcohol}}{CH_3-CH_2-OH}$$

64 kg of CaC_2 yield 46 kg of alcohol

1280 kg of CaC_2 yield (1280 kg × 46 kg)/64 kg

= 920 kg of C_2H_5OH

But the yield of alcohol is given as 80% of the theoretically possible amount. So the mass of alcohol actually obtained may be calculated as follows:

100% constitute 920 kg of C_2H_5OH

80% constitute $(80\% \times 920 \text{ kg})/100\% = 736$ kg of C_2H_5OH

This amount of C_2H_5OH constitutes 95%. Hence, we can determine the amount of alcohol produced in the given case:

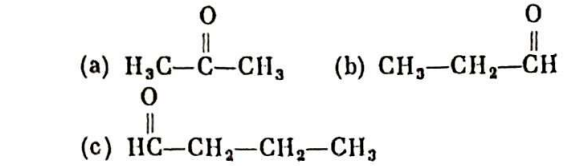
95% constitute 736 kg of C_2H_5OH

100% constitute $(100\% \times 736 \text{ kg})/95\%$

= 774.7 kg of C_2H_5OH

PROBLEMS AND EXERCISES

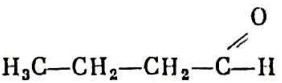
1. Which organic compounds are called aldehydes?
2. Which of the structural formulas corresponds to propanal:



3. Of the condensed linear structural formulas shown below which one is for 3-chloropentanal:

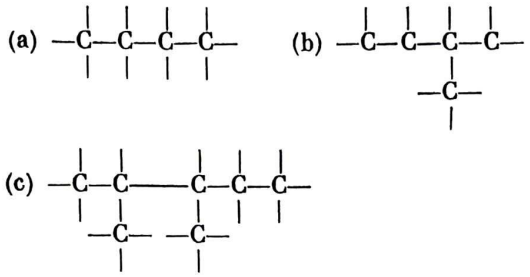
(a) $CH_3CHClCH_2CH_2CHO$ (b) $CH_3CH_2CHClCH_2CHO$
(c) $CH_3CHClCH_2CHO$ (d) $CH_3CH_2CCl(CH_3)CH_2CHO$

4. Why is it that the name 1-butanal for the aldehyde given below is not entirely correct?



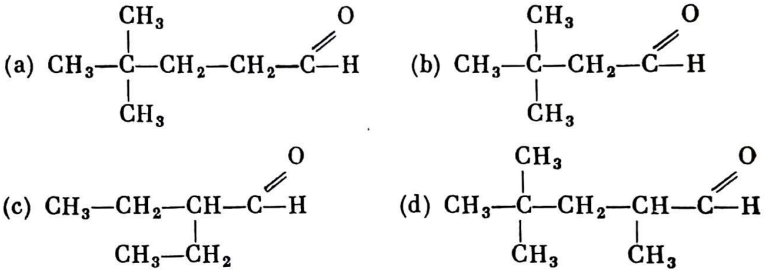
5. Which of the following general condensed structural formulas of aldehydes is correct: (a) R—CHO; (b) RCOH?
6. Which alcohols should be oxidized to obtain the following aldehydes: , $CH_3CH_2CH_2CHO$, CH_3CH_2CHO?
7. What are the industrial methods for the preparation of ethanal?
8. What is the Kucherov reaction?
9. How will you prepare an alcohol from the relevant aldehyde and vice versa?
10. What are polycondensation reactions? What are the similarities and what are the differences between the polymerization and polycondensation reactions?
11. Which type of reactions does the reaction leading to phenol-formaldehyde resins or bakelite belong to?

12. Write down the formulas and the names of the aldehydes having the following carbon skeletons:



13. Write down the structural formulas for the following compounds: (a) 2,2-dimethylbutanal, (b) 2,2,3-trimethylpentanal, (c) 2,4-dimethylpentanal and (d) 3-methylbutanal.

14. Name the following compounds according to the IUPAC nomenclature:



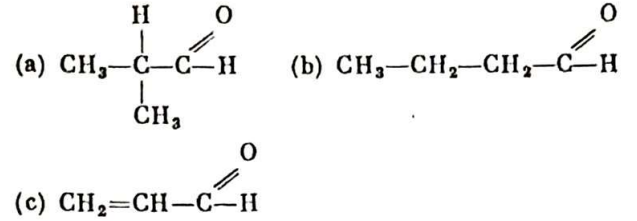
15. Write the condensed linear structural formulas for the aldehydes which are produced when the following alcohols are oxidized: (a) propyl, (b) *n*-butyl, (c) *n*-amyl.

16. Write the equations for the reactions that occur in the presence of nickel catalyst between hydrogen and (a) ethanal, (b) formaldehyde and (c) butyraldehyde.

17. Write the equations to represent catalytic oxidation of the following alcohols with oxygen of air at high temperatures: (a) 1-propanol, (b) methanol, and (c) ethanol.

18. Write the equations for the reactions which lead to the following aldehydes as a result of oxidation of the

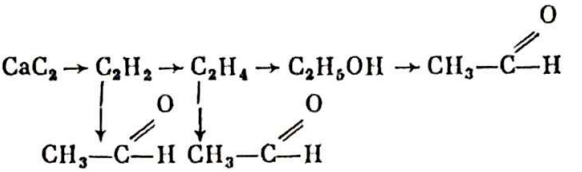
corresponding alcohols:



(a) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-\overset{\displaystyle O}{\overset{\|}{C}}-H$ (b) $CH_3-CH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-H$

(c) $CH_2=CH-\overset{\displaystyle O}{\overset{\|}{C}}-H$

19. Write the reaction equations involved in the following transformations:



$$CaC_2 \rightarrow C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_5OH \rightarrow CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H$$

$$C_2H_2 \rightarrow CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H \qquad C_2H_4 \rightarrow CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H$$

20. 22 kg of acetaldehyde can be prepared from 40 kg of technical-grade calcium carbide. Determine the mass percent of impurities in the carbide.

21. What volume of hydrogen is to be used to convert 11 kg of ethanal into ethanol?

22. How many millilitres of a formaldehyde solution which would have a density of 1.1 g/ml and contain 40% by mass of HCHO may be prepared by oxidizing 200 ml of an aqueous methyl alcohol of density 0.8 g/ml which contains 60% by mass of CH_3OH?

23. A compound containing 62% C, 27.6% O and 10.4% H (by mass) readily reduces cupric hydroxide to yield an acid. Derive the structural formula of this compound.

24. When 8.6 g of an aldehyde are oxidized with an ammoniacal solution of silver oxide, 21.6 g of silver are deposited. Calculate the molecular mass of the aldehyde. Write the structural formulas for the possible isomers and name each of them according to the Geneva nomenclature.

25. How many millilitres of a formaldehyde solution of density 1.06 g/ml which contains 20 mass percent of HCHO are to be added to an ammoniacal solution of silver oxide in order to obtain 1.08 g of silver?

26. 448 ml of acetylene were converted to acetaldehyde with a yield of 83%. Determine the mass of the metal

which is formed when this aldehyde is treated with an excess ammoniacal solution of silver oxide.

27. One test tube contains acetaldehyde and another ethylene glycol. How will you identify them with the aid of cupric hydroxide? Write the corresponding reaction equations.

28. Write the equation for the reaction that takes place between acetaldehyde and cupric hydroxide.

29. How many grams of cuprous oxide are formed when 55 g of an ethanal solution containing 40% by mass of CH_3COH are heated with cupric hydroxide?

30. 37 g of a mixture of formaldehyde and acetaldehyde were treated with silver oxide to yield 216 g of silver. Determine the mass percent of each aldehyde in the mixture.

31. When oxidized with an ammoniacal solution of silver oxide 0.5 g of technical-grade acetaldehyde yielded 2.16 g of a metal. Determine the mass percent of pure aldehyde in the technical-grade acetaldehyde.

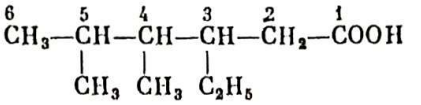
7.3 CARBOXYLIC ACIDS. SOAPS

Carboxylic acids are organic compounds which contain one or more carboxyl groups, $-\overset{\overset{O}{\parallel}}{C}-OH$.

The general formula for carboxylic acids is $R-\overset{\overset{O}{\parallel}}{C}-OH$, or RCOOH in the condensed form. Depending on the number of carboxyl groups in a molecule, carboxylic acids may be divided into monobasic, dibasic and others.

The trivial names for carboxylic acids have been derived from the names of common sources of these acids. For example, formic and acetic acids are derived from the Latin words *formicus* and *acetum*, which mean ant and vinegar (sources of these acids), respectively. Butyric acid smells like rancid butter (hence the word butyric coined from Latin *butyrum*, meaning butter). In this nomenclature the carbon atoms in the chain are designated by Greek letters α, β, γ, δ, etc., starting from the carbon adjacent to the carboxyl group in order to specify the positions of substituents, if any.

In the IUPAC nomenclature of aliphatic carboxylic acids, the names are derived from those of hydrocarbons with the same number of carbon atoms as in the acid. The ending 'e' of the alkane is replaced by 'oic acid'. Moreover, the longest carbon chain carrying the carboxyl group is selected and numbered from carboxyl carbon. Thus, the following saturated monobasic acid



will have the IUPAC name: 3-ethyl-4,5-dimethylhexanoic acid. The trivial names are, however, fairly commonly used. The first five members of the homologous series of monobasic carboxylic acids are given in Table 7.2.

Table 7.2 Names of Monobasic Carboxylic Acids

Molecular formula	Trivial name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
C_2H_5COOH	Propionic acid	Propanoic acid
C_3H_7COOH	Butyric acid	Butanoic acid
C_4H_9COOH	Valeric acid	Pentanoic acid

Among the saturated higher fatty acids, of great importance are the following two acids: palmitic, $C_{15}H_{31}COOH$ or $CH_3—(CH_2)_{14}—COOH$, and stearic, $C_{17}H_{35}COOH$ or $CH_3—(CH_2)_{16}—COOH$. Both these acids are solid substances. They are insoluble in water and are tasteless and odourless. They take part in the same reactions as do the other saturated carboxylic acids.

Alkali metal salts of these two acids are of special interest. Sodium and potassium salts are excellent detergents and form the basic component of any soap. Solid soaps are sodium salts of higher fatty acids, whereas liquid (or medicinal) soaps are potassium salts of these acids.

Oleic acid, $C_{17}H_{33}COOH$, and linoleic acid, $C_{17}H_{31}COOH$, which contains two double bonds, are the

most important unsaturated higher fatty acids. The double bond in a molecule of oleic acid is in the middle of the carbon chain:

$$H_3C-(CH_2)_7-CH=CH-(CH_2)_7-COOH$$

Oleic acid occurs in large amount in olive, almond and sunflower oils.

On reduction with hydrogen in the presence of catalysts, liquid oleic acid is converted into solid saturated stearic acid:

$$\underset{\text{oleic acid}}{C_{17}H_{33}COOH} + H_2 \xrightarrow[\text{catalyst}]{t} \underset{\text{stearic acid}}{C_{17}H_{35}COOH}$$

Linoleic acid, $C_{17}H_{31}COOH$ or $CH_3(CH_2)_4CH=CH-CH_2CH=CH(CH_2)_7-COOH$, occurs in large amounts in linseed and cottonseed oils. Oils containing unsaturated acids such as linoleic acid are widely used as protective coatings, since these acids are converted into a firm film under the action of oxygen in air.

Example 1. Name the following carboxylic acid according to the IUPAC nomenclature:

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2-COOH$$

Solution. Let us first number the carbon chain designating the carboxyl carbon by number 1. Next, we determine the locants for the substituents. The locant for methyl group is 4 and that for ethyl is 3. In this way, the IUPAC name for the given acid is 3-ethyl-4-methylpentanoic acid rather than 4-methyl-3-ethylpentanoic acid, because according to the IUPAC nomenclature, the substituents should be arranged in alphabetical order.

Example 2. A mass of 100 g of 0.408 *M* potassium hydroxide solution of density 1.02 g/ml was required to neutralize 10 g of an aqueous solution of a mixture of acetic acid and phenol. When an excess bromine water was added to 5 g of the same solution, 3.31 g of a precipitate were obtained. Determine the mass percents of acetic acid and phenol in the original solution.

Solution. 1. Of the two components in the mixture, only phenol reacts with bromine water. So we can calculate the mass of phenol in 5 g of the given solution:

$$C_6H_5OH + 3Br_2 = C_6H_3OBr_3 + 3HBr$$

331 g of $C_6H_3OBr_3$ come from 94 g of C_6H_5OH

3.31 g of $C_6H_3OBr_3$ come from $(3.31\ g \times 94\ g)/331\ g$
$= 0.94$ g of C_6H_5OH

That is,

5 g of the solution contain 0.94 g of phenol

So, 10 g of the solution will contain $(10 \times 0.94)/5$
$= 1.88$ g of phenol

2. Now we determine the volume occupied by 100 g of 0.408 *M* potassium hydroxide solution of density 1.02 g/ml:

$$V = \frac{100\ g}{1.02\ g/ml} = 98\ ml$$

3. So, the mass of KOH in a volume of 98 ml of 0.408 *M* solution may be calculated:

1000 ml contain 0.408 mole

98 ml contain $(98 \times 0.408)/1000 = 0.040$ mole

In terms of gram,

$$0.040\ mole = 0.040\ mole \times 56(g/mole) = 2.24\ g$$

4. The mass of alkali required to neutralize 1.88 g of phenol:

$$C_6H_5OH + KOH = C_6H_5OK + H_2O$$

94 g of C_6H_5OH require 56 g of KOH

1.88 g of C_6H_5OH require $(1.88\ g \times 56\ g)/94\ g$
$= 1.12$ g of KOH

5. To neutralize acetic acid, $2.24 - 1.12 = 1.12$ g of alkali will be needed.

6. Now we can finally calculate the mass of acetic acid that entered into reaction with 1.12 g of KOH:

$$CH_3COOH + KOH = CH_3COOK + H_2O$$

56 g of KOH consume 60 g of CH_3COOH

1.12 g of KOH consume $(1.12\ g \times 60\ g)/56\ g$
$= 1.2$ g of CH_3COOH

Therefore, 10 g of the given solution contain 1.88 g (or 18.8%) of phenol and 1.2 g (or 12%) of CH_3COOH.

Example 3. 500 ml of an aqueous solution contain 13.7 g of a mixture of oxalic and formic acids. 1.58 g of potassium permanganate are used to oxidize the solutes in 50 ml of this solution in the presence of sulphuric acid. Determine the molar concentrations of the acids in the solution.

Solution. 1. Let us first find out the total amount of oxalic and formic acids in 50 ml of the given solution:

500 ml contain 13.7 g of the mixture
50 ml contain 1.37 g of the mixture

2. Now the molar mass of potassium permanganate is equal to 158 g/mole. So, 1.58 g of $KMnO_4$ are equivalent to 1.58 g/158 (g/mole) = 0.01 mole.

3. Oxidation of the given acids proceeds according to the following equations:

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O \quad (1)$$

$$2KMnO_4 + 5HCOOH + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5CO_2 + 8H_2O \quad (2)$$

It follows from Eqs. (1) and (2) that in each case 2 moles of $KMnO_4$ and 5 moles of oxalic or formic acid take part in a reaction. This means that 0.01 mole of $KMnO_4$ will react with $0.01 \times 5/2 = 0.025$ mole of oxalic or formic acid.

4. Let us now determine how many moles of oxalic and formic acids are contained in 50 ml of the given solution. Let X be the number of moles of oxalic acid, then $(0.025 - X)$ is the number of moles of formic acid contained in 50 ml of the solution. Therefore, we can say that 1.37 g of the mixture consist of $90X$ g of oxalic acid and $46\ (0.025 - X)$ g of formic acid and we can write, $90X + 46\ (0.025 - X) = 1.37$, whence $X = 0.005$ mole. Hence 50 ml of the solution contain 0.005 mole of oxalic acid and $0.025 - 0.005 = 0.02$ mole of formic acid.

5. So, 500 ml of the solution contain 0.05 mole of oxalic acid and 0.2 mole of formic acid.

6. Let us finally determine the molar concentrations of (a) oxalic acid and (b) formic acid:

(a) 500 ml contain 0.05 mole of $H_2C_2O_4$

1000 ml contain $\frac{1000 \text{ ml} \times 0.05 \text{ mole}}{500 \text{ ml}} = 0.1$ mole of $H_2C_2O_4$

(b) 500 ml contain 0.2 mole of HCOOH

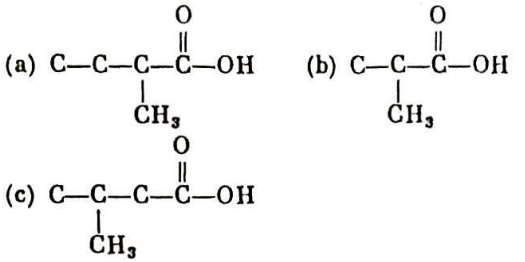
1000 ml contain $\frac{1000 \text{ ml} \times 0.2 \text{ mole}}{500 \text{ ml}} = 0.4$ mole of HCOOH

Therefore, we can conclude that 500 ml of the given solution contain 0.05 mole of oxalic acid and 0.2 mole of formic acid. Moreover, the solution will be 0.1 *M* $H_2C_2O_4$ and 0.4 *M* HCOOH.

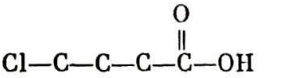
PROBLEMS AND EXERCISES

1. Which organic compounds belong to carboxylic acids?

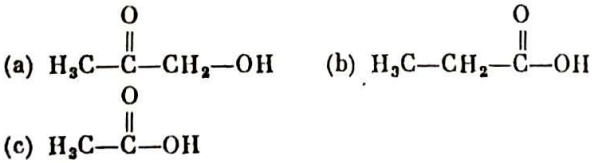
2. Of the structures displayed below which one is for 2-methylcarboxylic acid:



3. Which name: (a) 3-chlorobutanoic acid, (b) 1-chloropropanoic acid, or (c) 4-chlorobutanoic acid is to be given to the acid whose skeleton formula is given below:



4. Which of the following structural formulas corresponds to propanoic acid:



5. Write the structural formulas for the following saturated monobasic acids: (a) phenylpropanoic acid, $C_9H_{10}O_2$; (b) vinylethanoic acid, $C_4H_6O_2$; (c) butanoic acid $C_4H_8O_2$.

6. Will there be any reaction, if (a) sulphuric acid is added to magnesium acetate, (b) silicic acid is added to calcium acetate?

7. Which compound will be formed when ethanoic acid is reduced with hydrogen?

8. Which compound will be produced when oleic acid, $C_{17}H_{33}COOH$, is reduced with hydrogen?

9. Which saturated monobasic acid will be formed on oxidation of (a) ethanol, (b) methanol, (c) propionic aldehyde?

10. How is acetic acid prepared industrially? Name three main methods of preparation.

11. What reactions underlie qualitative identification of the carboxyl group?

12. Which compounds are produced during electrolysis of an aqueous solution of potassium acetate?

13. Which compounds are formed as a result of the following conversions:

$$CH_3CH_2OH \xrightarrow{+2O} \ldots \xrightarrow{+C_2H_5OH} \ldots \xrightarrow{+H_2O} \ldots$$

14. Which incombustible gas is evolved when methanoic acid decomposes under the action of a dehydrating agent?

15. Give the trivial names for the following compounds:

(a) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$ (b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-COOH$

(c) $CH_3-CH_2-CH_2-CH_2-CH_2-COOH$

(d) $CH_3-CH_2-CH_2-COOH$

16. Name the following carboxylic acids according to the trivial and IUPAC nomenclatures:

(a) CH_3-COOH (b) CH_3-CH_2-COOH

(c) $CH_3-CH_2-CH_2-COOH$

17. Draw the structural formulas for the isomers of valeric acid and give the trivial and IUPAC names for each of them.

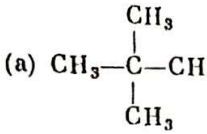
18. Draw the structural formulas for the following carboxylic acids: (a) 2-methylbutanoic, (b) 2,2-dimethylpropanoic, (c) 2,4,4-trimethylhexanoic, and (d) 3,5-diethyl-2,2,4,4-tetramethylheptanoic acids.

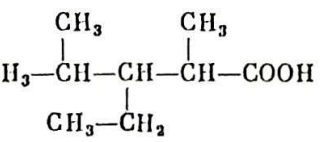
19. Write the reaction equations involved in the following conversions:

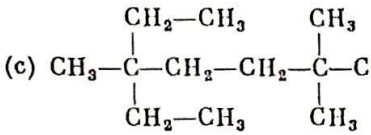
(a) $CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow CH_3{-}COH \rightarrow C_2H_5OH \rightarrow CH_3COOH$

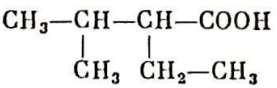
(b) $CaC_2 \rightarrow C_2H_2 \rightarrow CH_3COH \rightarrow CH_3COOH \rightarrow CH_3COOC_2H_5$

20. Name the following carboxylic acids according to the IUPAC nomenclature:

(a) 

(b) 

(c) 

(d) 

21. Will there be any reaction if (a) acetic acid is added to sodium sulphate, (b) ethanoic acid is added to sodium carbonate, (c) nitric acid is added to magnesium acetate? Write the relevant chemical equations.

22. Derive the formula for a carboxylic acid containing (by mass) 62% C, 27.6% O and 10.4% H. The vapour density of the compound with respect to hydrogen is 58. Write the structural formulas for the isomers of this saturated monobasic acid and name each of them according to the IUPAC nomenclature.

23. What volume of 40% HCHO solution (density 1.1 g/ml) is to be oxidized in order to get 100 ml of methanoic acid of density 1.3 g/ml which would contain 80% by mass of HCOOH?

24. How much ethyl alcohol solution which has a density of 0.8 g/ml and contains 96 mass percent of C_2H_5OH is to be taken in order to prepare 30 kg of acetic acid?

25. A volume of 100 ml of 0.5 *M* potassium hydroxide solution is used to neutralize 3.7 g of a saturated monobasic acid. Write the structural formula for this acid.

26. Neutralization of 30 g of a mixture of acetic acid and phenol solutions required 100 ml of 2 *M* sodium hydroxide solution. When the same mixture was treated with bromine water, 33.1 g of a precipitate were formed. Determine the mass percents of acetic acid and phenol in the given solution.

27. How many millilitres of acetic acid of density 1.064 which contains 60% by mass of CH_3COOH are to be taken to prepare 5 litres of 0.02 *M* solution?

28. Write down the reaction equations for preparing acetic acid from water, air, coal and limestone.

29. To prepare acetic acid, technical-grade calcium carbide containing 4% by mass of impurities was employed as the starting material. What mass of calcium carbide was used, if it is known that 240 g of 5.5 *M* potassium hydroxide solution of density 1.2 g/ml were required to neutralize the acid obtained.

30. 44.8 litres of ammonia were passed into 3 litres of 3 *M* acetic acid solution. How many grams of calcium carbonate can enter into reaction with the acid solution after ammonia has been passed into it?

31. How many grams of acid and how many grams of alcohol are to be taken for preparing 37 g of ethyl formate?

32. How many litres of hydrogen will enter into reaction with formic acid so that 10 g of the relevant aldehyde are formed?

33. Determine the mass of technical-grade acetic acid containing 10% by mass of impurities which is required to prepare 10.2 g of acetic anhydride.

34*. How many grams of 85% HCOOH solution and how many grams of sodium bisulphate are formed when 8 g of sodium hydroxide react with 5 litres of carbon monoxide measured at STP? Write down the chemical equations to represent the involved reactions.

35. Pure carbon monoxide is prepared by decomposition of formic (methanoic) acid in the presence of concentrated sulphuric acid as a dehydrating agent. How many grams of formic acid which contains 85% by mass of HCOOH are to be taken in order to prepare 20 litres of carbon monoxide at STP?

36. On fast heating sodium formate loses hydrogen to yield a salt of a dibasic carboxylic acid which when allowed to react with calcium nitrate gives a white precipitate. Write the equations for the reactions that take place and the structural formulas of the salts.

37. State whether the properties of the hydroxyl group in ethanol, phenol and ethanoic acid are the same or not. Write the reaction of each of these with (a) metals, (b) alkalies and (c) bromine water. How can a mixture of these three organic compounds be separated?

38. An unsaturated monobasic acid was hydrogenated with 2.24 litres of hydrogen to produce 28.4 g of a saturated monobasic acid containing (by mass) 76% C, 12.7% H and 11.3% O. What is the acid that was hydrogenated?

39. Write the chemical equations to represent the reactions between (a) palmitic acid ($C_{15}H_{31}COOH$) and calcium hydroxide, (b) stearic acid ($C_{17}H_{35}COOH$) and potassium hydroxide, (c) sodium stearate and magnesium chloride, and (d) potassium palmitate and calcium hydroxide.

40. How much palmitic acid may be obtained by reacting liquid green soap containing 29.4 kg of potassium palmitate with a sulphuric acid solution?

41. How many millilitres of sulphuric acid which has a density of 1.4 g/ml and contains 40% by mass of H_2SO_4 will be needed in order to extract stearic and palmitic acids from 40 g of solid sodium soap which contains 69.5% by mass of sodium stearate?

42*. When 11.4 g of an unknown oxygen-containing organic compound are oxidized, 15 g of a monobasic organic acid are produced. To neutralize this acid, 59.4 ml of a potassium hydroxide solution having a density of 1.18 g/ml and containing 20 mass percent of KOH were used. Which compound was taken for oxidation?

43*. 182 ml of 10% NaOH solution (density 1.1 g/ml) were required to neutralize 24.4 g of a mixture of acetic and formic acids. Determine the mass percents of these two acids in the mixture.

44*. A volume of 76.92 ml of a sodium hydroxide solution which has a density of 1.04 g/ml and contains 5% by mass of NaOH was required to neutralize 125 g of a mixture of ethyl alcohol and acetic acid in hexane.

When the same amount of the mixture was treated with an excess sodium, 3.36 litres of a gas were liberated. Calculate the mass percent of ethyl alcohol in the original mixture.

45. What volume of hydrogen measured at standard conditions will evolve, when 8 g of magnesium are treated with acetic acid?

46. What volume of a sodium hydroxide solution which has a density of 1.09 g/ml and contains 20% by mass of NaOH is required to neutralize 500 g of acetic acid containing 20% by mass of CH_3COOH?

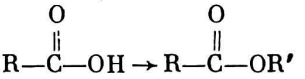
47. How many kilograms of 85% CH_3COOH solution may be prepared by oxidizing 2 tons of acetaldehyde?

48. How many grams of formic acid had been oxidized by an ammoniacal solution of silver oxide, if this reaction yielded 0.1 mole of silver? What volume of carbon dioxide was evolved as a result of the oxidation?

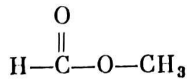
49. 100 g of a sodium hydroxide solution containing 5% by mass of NaOH were added to 200 ml of an acetic acid solution of density 1.1 g/ml containing 10% by mass of CH_3COOH. Find out whether it is possible now to dissolve 2 g o limestone in the resultant acetic acid solution.

7.4 CARBOXYLIC ESTERS AND FATS

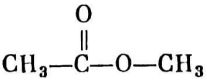
Derivatives which are formed from carboxylic acids by replacing in them the hydroxyl part of the carboxylic groups by an alkoxy group of an alcohol are known as carboxylic esters or simply esters:



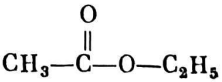
The trivial names of esters are formed from the alkyl or aryl part of the alcohol and the acid part of the acid, which constitute the ester by adding the ending 'ate' as exemplified below:



methyl formate (methyl methanoate)



methyl acetate (methyl ethanoate)



ethyl acetate (ethyl ethanoate)

Likewise, the IUPAC names of esters are formed from the alkyl or aryl part of the alcohol and from the acid part by replacing 'oic acid' in the IUPAC names of the acids by 'oate'. In the above examples and below in this Section these are shown in parentheses.

Esters are prepared by reacting alcohols with acids. This reaction is called *esterification*:

$$C_3H_7OH + HO{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \rightarrow \underset{\text{propyl acetate (propyl ethanoate)}}{C_3H_7{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3} + H_2O$$

One of the most important chemical properties of esters is that they undergo hydrolysis to yield the starting materials, that is, alcohols and acids. The reaction of hydrolysis of esters is called *saponification*. Saponification can take place under the action of aqueous mineral acids or alkalies:

$$\underset{\text{methyl propionate (methyl propanoate)}}{CH_3{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_3} + HOH \rightarrow \underset{\text{propionic acid (propanoic acid)}}{CH_3{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}OH} + \underset{\text{methyl alcohol (methanol)}}{CH_3OH}$$

On reduction esters yield two alcohols as follows:

$$\underset{\text{ethyl formate (ethyl methanoate)}}{H{-}\overset{\overset{O}{\|}}{C}{-}O{-}C_2H_5} + 2H_2 \rightarrow \underset{\text{methyl alcohol (methanol)}}{CH_3OH} + \underset{\text{ethyl alcohol (ethanol)}}{C_2H_5OH}$$

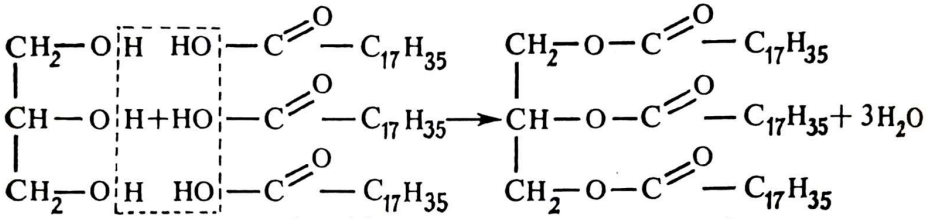
Esters formed from the trihydric alcohol, glycerol (trade name glycerine) and higher carboxylic acids are called *fats*:

$$\begin{array}{l} CH_2{-}O{-}COR \\ | \\ CH{-}O{-}COR' \\ | \\ CH_2{-}O{-}COR'' \end{array}$$

where R, R′, and R″ are the hydrocarbon residues of the higher fatty acids. Fats generally contain monobasic acids with straight carbon chains containing from 4 to 24 carbon atoms. Acids that form fats are either satur-

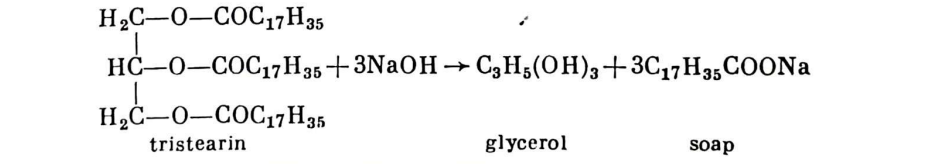
ated, or unsaturated. Acids which are most commonly used in fats are butyric (C_3H_7COOH), palmitic ($C_{15}H_{31}COOH$), stearic ($C_{17}H_{35}COOH$), oleic ($C_{17}H_{33}COOH$), linoleic ($C_{17}H_{31}COOH$), and several other acids.

Since the molecule of a fat contains three acid residues which form three ester groups by reacting with three alcoholic hydroxyl groups of a glycerol molecule, fats are also known as *triglycerides*. For example, the fat which contains three residues of stearic acid is called *tristearin*:



Triglycerides which contain three residues of a single acid occur only in a few fats, and can be prepared synthetically. If a fat contains three different acids, then mixed triglycerides are formed. For example, butter consists mainly of three different acids, oleic, palmitic and butyric acids. In this case the name of the fat is constructed on the basis of the names of these acids, namely, oleopalmitobutyrate.

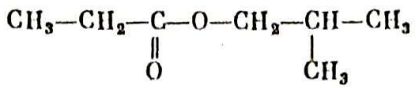
If fats are hydrolyzed with alkalies, then glycerol and salts of higher carboxylic acids, called soaps, are formed. For example:



Example 1. Write the structural formula of 2-methylpropyl propanoate.

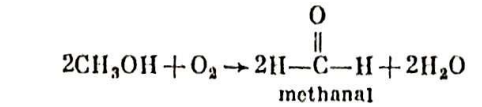
Solution. It follows from the name that the given ester is formed from isobutyl alcohol and propionic acid. Hence

the structure:

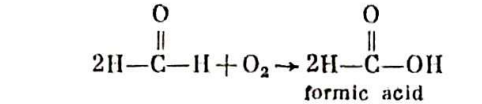


Example 2. How is methyl formate prepared from methanol? Write down the equations for the respective reactions.

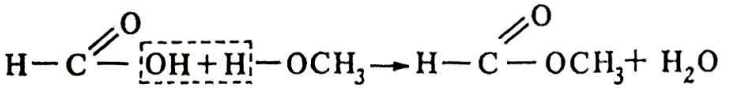
Solution. Methyl formate is an ester formed from methyl alcohol and formic acid. First, methanol can be oxidized to formaldehyde as follows:



Next, methanal is catalytically oxidized to yield formic acid:

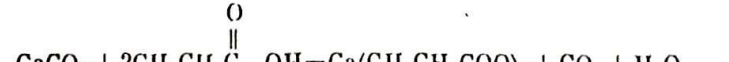


Finally, methyl formate is prepared as follows:



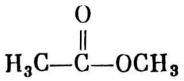
Example 3. Two compounds have the same molecular formula, $C_3H_6O_2$. One of these displaces carbon dioxide from calcium carbonate, while the other does not react with this carbonate, but reacts with sodium hydroxide on heating to yield an alcohol and a salt. What are these compounds? Write down the equations for the reactions that take place.

Solution. Only an acid is capable of displacing CO_2 from calcium carbonate. So one of the compounds is propionic acid. Its reaction with $CaCO_3$ is shown below:

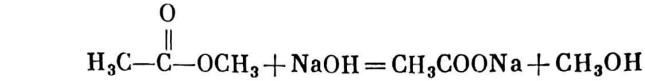


Next, an alcohol and a salt may be formed by heating $C_3H_6O_2$ with NaOH only when $C_3H_6O_2$ is an ester having

the following structure



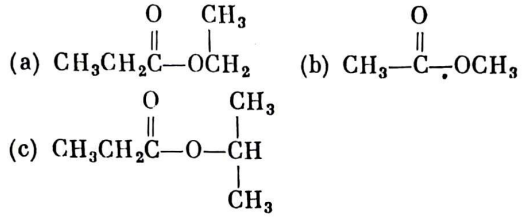
This is methyl acetate (or methyl ethanoate) which reacts with NaOH according to the following equation:



The products are methyl alcohol and sodium acetate.

PROBLEMS AND EXERCISES

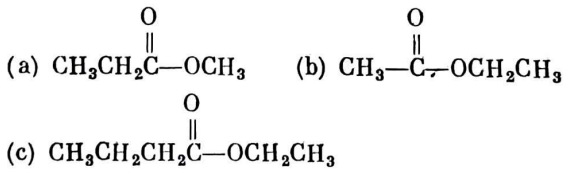
1. What alcohols were used to produce the following esters:



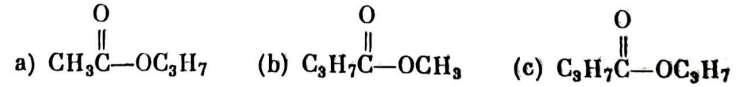
2. Among the systematic names given below which one is correct for the ester $CH_3CH_2COO(CH_2)_2CH_3$: (a) 1,1-dimethyl propanoate, (b) propyl propanoate, (c) methyl propanoate?

3. Which acids are the following esters made of: (a) ethyl pentanoate, (b) methyl butyrate, (c) methyl acetate, (d) propyl formate?

4. Name the esters displayed below according to the trivial system of nomenclature:



5. Name the following esters according to the IUPAC nomenclature system:



6. Which reactions are termed as saponification reactions?

7. What are the products obtained when (a) methyl acetate is hydrolyzed? (b) methyl propionate is reduced with hydrogen?

8. What are soaps? How are they prepared?

9. What is the composition of soap produced when tristearin is hydrolyzed with potassium hydroxide?

10. What are synthetic detergents? Which valuable products do they substitute for?

11. Write the expanded structural formula for the ester, $CH_3(CH_2)_2COO(CH_2)_2CH_3$. Name it according to both trivial and IUPAC nomenclatures.

12. Set up the equations to represent the reactions for the preparation of the following esters: (a) propyl acetate, (b) ethyl formate, (c) methyl propionate, (d) methyl acetate.

13. Write down the equations for the preparation of the following esters: (a) methyl formate, (b) ethyl propanoate, (c) propyl propanoate, (d) propyl formate.

14. Write down the equations involved in the following conversions:

(a) $CH_2{=}CH_2 \rightarrow CH_3\overset{\overset{O}{\|}}{C}{-}OC_2H_5 \rightarrow C_2H_5OH \rightarrow CH_2{=}CH_2$

(b) $C_2H_2 \rightarrow CH_3OH \rightarrow C_2H_5OH \rightarrow CH_3COOH \rightarrow CH_3COOCH_3$

15. What products are formed when (a) ethyl formate is hydrolyzed, (b) methyl propanoate is reduced with hydrogen? Write the equations to represent the reactions that take place.

16. How many grams of methyl formate can be prepared from 20 g of an aqueous alcohol solution, containing 80% by mass of alcohol, and 57.5 g of an aqueous acid solution which contains 40% by mass of the acid, if the yield of the ester is 90%?

17. 2.3 g of formic acid react with an alcohol to yield 3.7 g of an ester. Write the structural formula of the produced ester and name it.

18. How many millilitres of a propyl alcohol solution of density 1.1 g/ml which would contain 60% by mass of

C_3H_7OH and how many millilitres of an ethyl alcohol solution of density 0.8 g/ml which would contain 90% by mass of C_2H_5OH may be obtained when 10.2 g of ethyl propionate are reduced?

19. 9.8 ml of an ester of density 0.9 g/ml reacted with 20 g of a sodium hydroxide solution containing 20% by mass of NaOH. Ethyl ester of which acid was subjected to saponification?

20. 50 ml of 2 *M* NaOH solution are needed to hydrolyze 7.4 g of an unknown ester of formic acid. Which ester was taken for the reaction?

21*. Determine the mass percents of methyl acetate and of methyl propionate in a mixture from the following data: 35.7 g of 5 *M* caustic soda solution (density 1.19 g/ml) were required to hydrolyze 12 g of this mixture.

22*. By reacting a mixture of acetic and formic acids with 23 ml of absolute ethyl alcohol of density 0.8 g/ml in the presence of a mineral acid, 32.4 g of a mixture of esters were formed. Determine the mass percents of formic and acetic acids in the mixture.

23*. To hydrolyze 25 g of a mixture of ethyl formate and ethyl acetate, 65.67 ml of 20% NaOH solution (density 1.22 g/ml) were used. After the hydrolysis was over, the excess alkali was neutralized with 50 ml of 1 *M* sulphuric acid solution. Calculate the mass percents of the esters in the original mixture.

24. Find out the molecular formula of an ester, if 80 g of a sodium hydroxide solution which contains 10% by mass of NaOH are needed for saponification of 12 g of this ester.

25. How many grams of the relevant acid and alcohol, respectively, will be obtained when 80 g of methyl propanoate are hydrolyzed?

26. Outline the saponification of the fat displayed below

$$\begin{array}{l} CH_2{-}O{-}COC_{15}H_{29} \\ | \\ CH{-}O{-}COC_{17}H_{33} \\ | \\ CH_2{-}O{-}COC_{15}H_{31} \end{array}$$

(a) with potassium hydroxide and (b) with water.

27. Draw the structural formula of the ester formed when glycerol reacts with three different acids, namely palmitic, stearic and butyric acids.

28. How many kilograms of the fat, tributyrate, will be formed when 9.2 g of glycerol react with butyric acid?

29. What mass of triolein should be hydrolyzed in order to get 84.6 g of oleic acid?

30. How many millilitres of 2 *M* sodium hydroxide solution are to be used to hydrolyze tristearate in order to get 15.3 g of sodium stearate?

31. What volume of hydrogen should be used to convert 200 kg of the liquid fat, triolein, into solid tristearin?

32. How many grams of ethyl alcohol are to be taken in order to prepare 35.6 g of ethyl acetate, if the yield of the product is 80% of the theoretical amount?

33. How many grams of acetic acid are required to carry out esterification, if it is known that this results in 118.8 g of ethyl acetate, the yield being 90% of the theoretical amount?

34. Find out the molecular formula of an ester from the following data: saponification of 12 g of this ester requires 80 g of 10% NaOH solution.

35. For the hydrolysis of 5.6 g of a mixture of ethyl acetate and ethyl formate, 25.96 ml of a sodium hydroxide solution of density 1.08 g/ml containing 10% by mass of NaOH were used. Determine the mass percents of the esters in the mixture.

36. What volume of hydrogen at standard conditions will be required in order to convert 13.26 kg of the fat, trioleate, into a solid fat. The production loss for hydrogen is 15%.

37. How many kilograms of glycerol may be obtained by hydrolyzing 17.8 kg of the natural fat, glyceryl tristearate, containing 3% by mass of impurities?

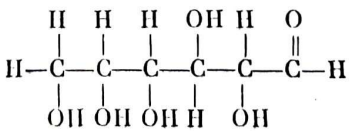
38. How many grams of methyl formate may be prepared from 40 g of the alcohol containing 96% by mass of alcohol and 60 g of the acid, which contains 40% by mass of acid? The yield of the product is 90% of the theoretical amount.

7.5 CARBOHYDRATES (SUGARS)

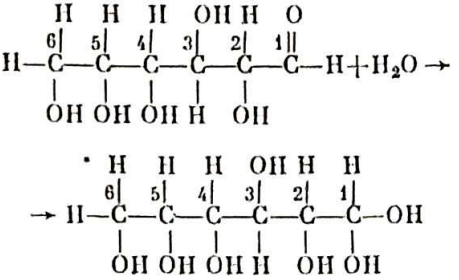
Carbohydrates are classified into two groups: (a) simple carbohydrates (or simple sugars) and (b) complex carbohydrates (or complex sugars).

Simple carbohydrates (also called monosaccharides or monoses) are those carbohydrates which are not capable of being hydrolyzed. Monosaccharides are further divided into aldoses and ketoses depending upon whether aldehyde or keto group is present in their structures. Monoses are also classified depending on the number of carbon atoms in their molecules: C_4 sugars are called tetroses, C_5 sugars pentoses, C_6 sugars hexoses and so on. Monoses can contain from three to ten carbon atoms.

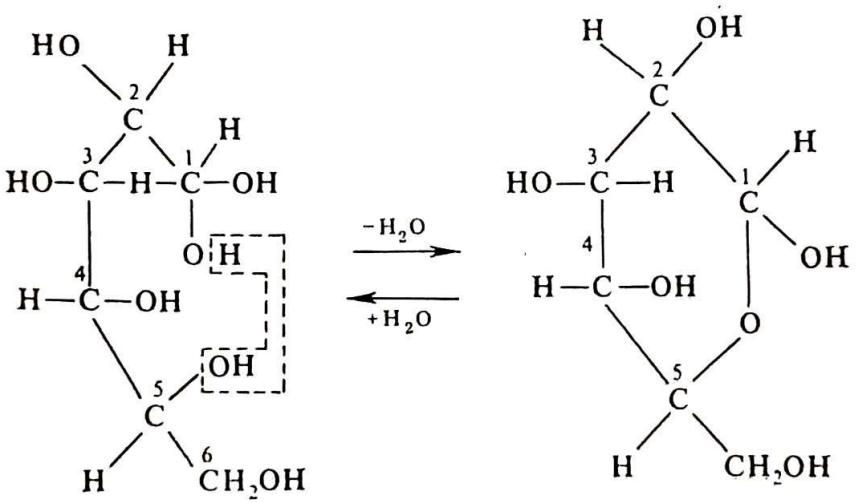
Complex carbohydrates are such carbohydrates which can be hydrolyzed to simple carbohydrates. They include oligosaccharides and polysaccharides. Upon hydrolysis, one oligosaccharide molecule produces several molecules of monosaccharides, whereas one polysaccharide molecule gives a huge number of such monosaccharide molecules. *Glucose* and *fructose* belong to the most abundant monosaccharides. These two have the same molecular formula, $C_6H_{12}O_6$. On the basis of a series of reactions it was established that the glucose molecule exhibits the properties of both aldehyde and polyhydric alcohol. Glucose is, therefore, also called *aldehyde alcohol.* Like polyhydric alcohols, glucose forms a bright-blue solution with cupric hydroxide. On heating with an ammoniacal solution of silver oxide, glucose gives a positive "silver mirror test" which proves that it contains an aldehyde group. With acetic acid, glucose gives an ester which contains five acetate groups. The structural formula for glucose may thus be written as follows:



Glucose can readily add water molecule to the aldehyde group, thus transforming into an unstable hydrate form:

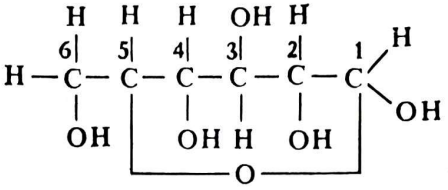


Since the carbon chain in a glucose molecule (and in any monosaccharide molecule in general) is not straight, but bent, water is removed easily as the hydroxyl groups of the first and the fifth carbon atoms in the hydrate form come close to each other. The result is a new form of glucose, i.e. a cyclic form which is tautomeric (reversible) to the linear form:

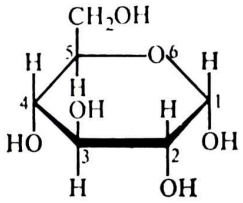


The cyclic tautomeric forms of monosaccharides are represented in two different ways. In the first case, the carbon chain of a monosaccharide is arranged in a straight line, while the bonding between oxygen and two carbon

atoms, C_1 and C_5, is shown in the form of a bridge:



In the second case, the whole molecule is depicted in the form of a spatial structure:



Thus, monosaccharides can exist not only in the acyclic forms, but in the form of cyclic structures as well.

Disaccharides are the most important oligosaccharides. These are complex sugars each molecule of which decomposes upon hydrolysis into two monosaccharide molecules. Disaccharides have a complex structure. They are the derivatives of the cyclic forms of monosaccharides. Sucrose (also called beet sugar or cane sugar), $C_{12}H_{22}O_{11}$, is of the utmost importance among the disaccharides. Sucrose does not exhibit reactions which are characteristic of monosaccharides, since it lacks free aldehyde or keto group. However, it readily hydrolyzes to yield a mixture of glucose and fructose:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H_2SO_4} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Polysaccharides are complex sugars each molecule of which decomposes upon hydrolysis to produce a large number of monosaccharide molecules, this number varying between 30 thousand and 400 million. Polysaccharides do not form true solutions, do not have a sweet taste, nor do they form visible crystals. The general molecular formula of the polysaccharides may be represented as $(C_6H_{10}O_5)_n$. All of them consist of glucose units connected

with one another. *Starch* and *cellulose* are the most important polysaccharides.

Starch does not show reactions which are characteristic of monosaccharides. It does not possess reducing properties, that is, does not form a red precipitate of cuprous oxide. Under the action of mineral acids starch is hydrolyzed to glucose:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$$

A qualitative test for starch is its reaction with iodine solution which turns deep blue in the presence of starch. Analytical chemistry makes use of this reaction to detect molecular iodine.

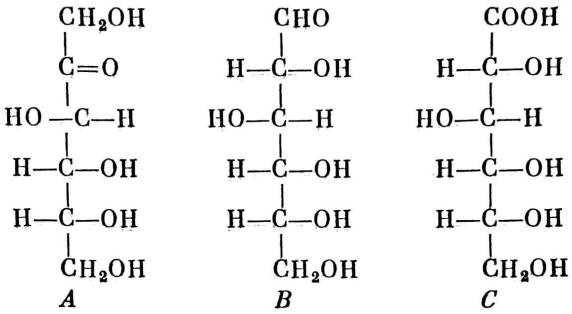
Cellulose is the chief constituent part of any plant cell and imparts mechanical strength to the plant tissue. Cotton fibers represent nearly pure cellulose (90-95%). Various types of wood contain 40 to 60% cellulose. Pure cellulose is a solid fibrous compound which dissolves neither in water, nor in ordinary solvents. Only in Schweitzer's reagent, which is a solution of cupric hydroxide in concentrated ammonia solution, does it dissolve. Unlike a starch molecule which may have both linear and branched forms, cellulose molecules have linear structures. The molecular mass of a cellulose molecule may reach several million units. The chemical properties of cellulose are due to the presence of the hydroxyl groups in it. Cellulose, thus, can form both ethers and esters. For example, when cellulose is allowed to react with a mixture of nitric and sulphuric acids, nitric esters are formed. Depending upon the reaction conditions, mono-, di-, and trinitrocellulose may be prepared:

$$\left[C_6H_7O_2(OH)_3\right]_n + 3nHNO_3 \xrightarrow{H_2SO_4} \left[C_6H_7O_2(O{-}NO_2)_3\right]_n + 3nH_2O$$

When cellulose is treated with a mixture of acetic and sulphuric acids, cellulose triacetate is produced:

$$\left[C_6H_7O_2(OH)_3\right]_n + 3nHOOCCH_3 \rightarrow \left[C_6H_7O_2(O{-}OCCH_3)_3\right]_n + 3nH_2O$$

Example 1. Of the structural formulas displayed below which one is for a ketohexose?

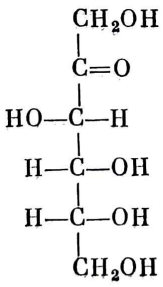


A *B* *C*

Solution. Formulas *A* and *B* belong to hexose, but only *A* corresponds to a ketohexose, because it has a keto group, $\rangle C{=}O$, whereas formula *B* contains an aldehyde group, $-C(=O)-H$. The third structural formula, *C*, represents gluconic acid.

Example 2. Is it possible to oxidize fructose to an acid in the skeleton of which all the carbon atoms of the reactant would be retained?

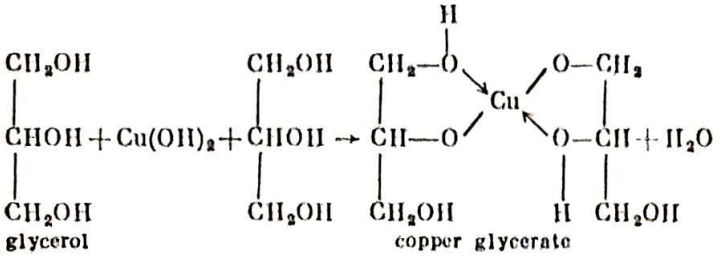
Solution. Fructose is a ketone alcohol. Its structural formula is:

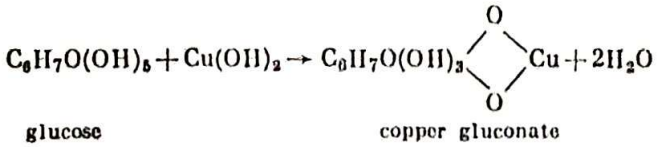


Fructose cannot be oxidized in such a way as to retain in the produced acid all the six carbon atoms of the starting material, because carbonyl group can be oxidized to carboxyl one only when the former is at the end of a carbon chain.

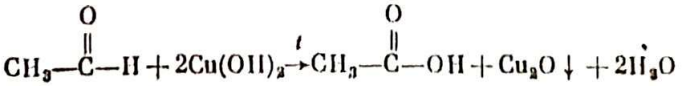
Example 3. Three bottles contain solutions of glycerol, acetaldehyde and glucose, respectively. How will you identify the content of each bottle? What is the most rational way of the analysis? Write down the equations for the involved reactions.

Solution. To test for glucose, glycerol and acetaldehyde, we add $Cu(OH)_2$ to each bottle. Cupric hydroxide should be freshly prepared. Glycerol and glucose each forms a blue solution with $Cu(OH)_2$. This proves that these two compounds are polyhydric alcohols:



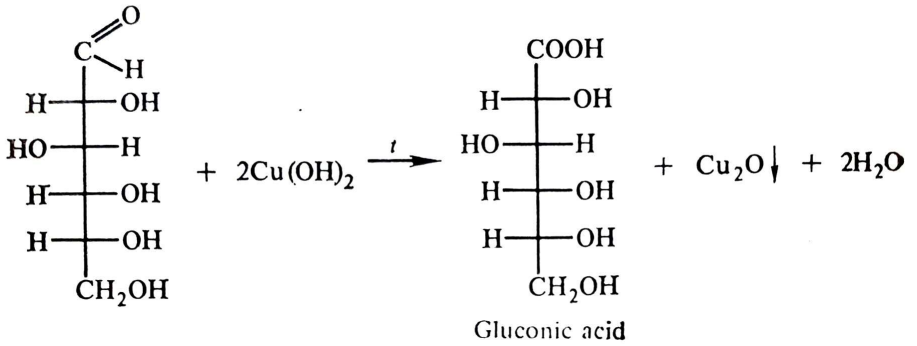


Acetaldehyde does not form any blue solution when treated with $Cu(OH)_2$. However, when the mixture of acetaldehyde and $Cu(OH)_2$ is heated, a precipitate, Cu_2O, is formed:



Next, we heat the test tubes containing the complex salts, copper glycerate and copper gluconate. A solution of glucose and $Cu(OH)_2$ changes its colour due to the forma-

tion of a precipitate, Cu_2O, following the equation:



Gluconic acid

There is no change in colour in the test tube containing glycerol and $Cu(OH)_2$.

Example 4. Formation of glucose during photosynthesis may be represented by the following chemical equation:

$$6CO_2 + 6H_2O + 2692\ kJ \rightarrow C_6H_{12}O_6 + 6O_2$$

Each square centimeter of the earth's surface receives nearly 2 J of solar energy per minute. How much time will 10 leaves take to form 0.9 g of glucose, if each leaf has an area of 10 cm^2 and only 10% solar energy is utilized in the photosynthesis?

Solution. The energy required for the photosynthesis of 0.9 g of glucose may be calculated as follows:

180 g of $C_6H_{12}O_6$ require 2692 kJ

$$0.9\ g\ of\ C_6H_{12}O_6\ requires\ \frac{0.9\ g \times 2692\ kJ}{180\ g} = 13.46\ kJ$$

Now the solar energy received by the total surface area of 10 leaves for one minute is 2 (J/min) × 10 cm^2 × 10 leaves = 200 J/min. But the useful solar energy for 10 leaves should be:

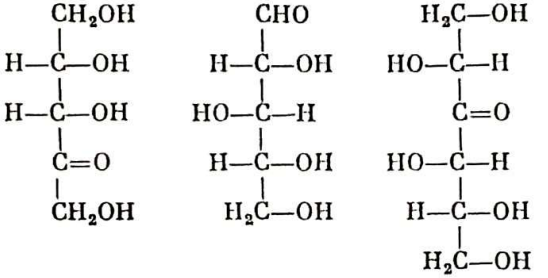
$$100\% \equiv 200\ J/min$$

$$10\% \equiv \frac{10\% \times 200(J/min)}{100\%} = 20\ J/min$$

So assimilation of 13.46 kJ of solar energy proceeds within 13.46 kJ/20 (J/min) = 673 min = 11 h 13 min.

PROBLEMS AND EXERCISES

1. Which organic compounds belong to carbohydrates? Where does this name come from? How are they classified?
2. Which reactions may prove that glucose is an aldehyde alcohol?
3. What types of fermentation does glucose yield?
4. What is the biological role of glucose?
5. Explain the difference in the structures of glucose and fructose molecules.
6. Which functional groups are there in a molecule of glucose?
7. Among the structural formulas displayed below which one is for a ketopentose:



8. Which of the following carbohydrates can be hydrolyzed: (a) fructose, (b) starch, (c) sucrose, (d) glucose?
9. Which carbohydrates listed below exhibit "silver mirror" test: (a) cellulose, (b) glucose, (c) fructose?
10. Which of the following carbohydrates can dissolve cupric hydroxide? (a) sucrose, (b) fructose, (c) glucose, (d) starch?
11. Of the following carbohydrates which one contains the largest number of carbon atoms: (a) cane sugar, (b) fructose, (c) glucose?
12. What are the similarities and what are the differences in the structures of starch and cellulose? Why is it not possible to get fibers from starch?
13. Name the qualitative tests for starch, cellulose and glucose.
14. During the preparation of sugar from beet the solution is treated with calcium hydroxide and carbon dioxide. Why?
15. Write down the equations to represent the reactions

that take place during lactic and alcoholic fermentations of glucose. Calculate the volume of carbon dioxide which is formed at STP when 360 g of glucose are subjected to alcoholic fermentation.

16. Write the equation for the complete oxidation of glucose. Calculate the volume of carbon dioxide formed when 2 moles of glucose are completely oxidized.

17. What mass of silver oxide containing 5% impurities will be required to oxidize 0.5 mole of glucose to gluconic acid?

18. How many litres of 95% C_2H_5OH solution (density 0.79 g/ml) will be produced by alcoholic fermentation of 36 kg of glucose?

19. Write down the structural formula of arabinose (gum sugar), $C_5H_{10}O_5$, if it is known that this is an aldehyde alcohol. How does this monose behave towards an ammoniacal solution of silver oxide?

20. 9 g of glucose react with cupric hydroxide in an alkaline medium to yield copper gluconate according to the following equation:

$$C_6H_7O(OH)_5 + Cu(OH)_2 \rightarrow C_6H_7O(OH)_3\begin{matrix}O\\ \diagup\ \diagdown\\ Cu\\ \diagdown\ \diagup\\ O\end{matrix} + 2H_2O$$

What other organic compounds react with cupric hydroxide in a similar way? How many grams of copper gluconate are formed in the given case?

21*. A mass of 36.6 g of a mixture of glycerol, phenol and glucose was treated with cupric hydroxide. As a result, 38 g of a blue precipitate were formed. When the same mixture is treated with silver oxide, 21.6 g of silver precipitate are produced. Determine the mass percents of the three compounds in the mixture.

22. What volume of hydrogen gas will be used to reduce 36 g of glucose and how many grams of a hexahydric alcohol called sorbitol will be produced as a result of this reduction?

23. How many litres of air will be needed at standard conditions in order to produce as much carbon dioxide as required to prepare 0.9 g of glucose in the process of photosynthesis? The carbon dioxide molecules constitute 0.03% of the all air molecules.

24. How many tons of sugar beet which contains 20% by mass of sucrose will have to be hydrolyzed in order to prepare 1 ton of glucose?

25. Write the equations to represent preparation of the following esters of cellulose: (a) trinitrocellulose, and (b) cellulose triacetate.

26. How will you account for a high strength of cellulose and its insolubility in water? Write down the equations to represent the reactions that characterize the properties of cellulose.

27. Write down the equations for the reactions that confirm the biological importance of starch and the essence of its conversion in human organism.

28. What is the value of n in the molecular formula for a cotton fiber whose molecular mass equals 1,750,000? What volume of a nitric acid solution which has a density of 1.3 g/ml and contains 50 mass percent of HNO_3 will be required for nitrating 20 g of the cotton fiber to trinitrocellulose?

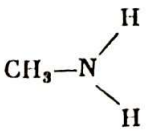
29. Write down the equations for the reactions that can be used to prepare the following compounds from cellulose: (a) ethanol, (b) ethyl acetate, (c) cellulose triacetate.

8
ORGANIC COMPOUNDS CONTAINING NITROGEN

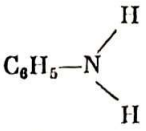
8.1 AMINES, AMINO ACIDS AND PROTEINS

Derivatives of ammonia obtained by replacing one, two or all three hydrogen atoms in an ammonia molecule by hydrocarbon residues are known as amines.

Depending upon the nature of the hydrocarbon residues, amines are classified as aliphatic, aromatic or aliphatic-aromatic amines:



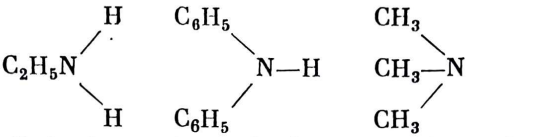
methylamine (aliphatic amine)



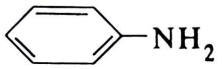
phenylamine (aromatic amine)

methylaniline (aliphatic-aromatic amine)

They are also classified as primary, secondary or tertiary amines depending on the number of hydrogen atoms that are replaced by hydrocarbon residues in the ammonia molecule. For example:



Let us have a look at the primary aromatic amine, aminobenzene, $C_6H_5NH_2$, which is more familiar as aniline

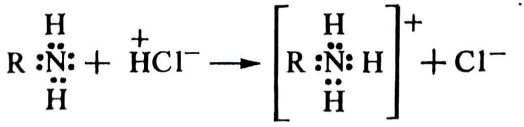


Unlike aliphatic amines, aromatic amines exhibit weak basic properties, because an aromatic ring reduces the basic character of an amino group, $-NH_2$.

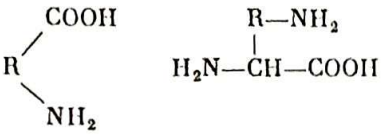
The unshared pair of electrons at the nitrogen atom of an aromatic amine interacts with the π electrons of the benzene ring and is shifted towards this ring. As a result, the electron density at the nitrogen atom is reduced, and hence, the latter more weakly holds hydrogen ions which, in turn, bind the hydroxyl ions present in a solution. Aromatic amines are, therefore, weak bases. With acids aniline forms salts as shown below:

$$\underset{\text{aniline}}{C_6H_5NH_2} + HCl \rightarrow \underset{\text{aniline hydrochloride}}{C_6H_5N^+H_3Cl^-}$$

The structures of amine salts are analogous to those of ammonium salts, that is, the complex cation is bonded to the chloride ion by an electrovalent bond. Formation of the amine salts can be expressed in terms of electronic formulas:

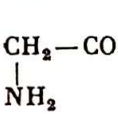
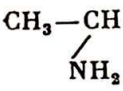
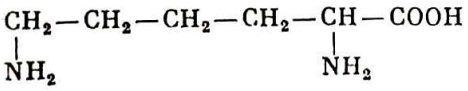
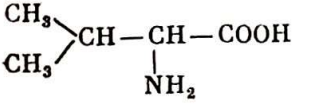
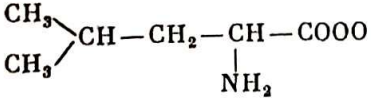


Amino acids are the derivatives of carboxylic acids in which one or more hydrogen atoms of the alkyl part is/are replaced by one or more amino groups:



The rational names for the amino acids have been derived from the names of the corresponding carboxylic acids, by adding the prefix 'amino'. In this nomenclature the carbon atom containing the amino group is designated by a Greek letter to indicate the position of this group with respect to the carboxylic group. Empirical or trivial names are often used for the amino acids (Table 8.1).

Table 8.1 Rational and Empirical Names of Amino Acids

Molecular formula	Rational name	Empirical name
	α-Aminoacetic acid	Glycine
	α-Aminopropionic acid	Alanine
	α,ε-Diaminocaproic acid	Lysine
	α-Aminoisovaleric acid	Valine
	α-Aminoisocaproic acid	Leucine

Since amino acids contain two functional groups having opposite properties (the acidic carboxylic group and the

basic amino group), they can exhibit both acidic and basic properties simultaneously.

Amino acids react with alkalies as acids to form salts:

$$H_2NCH_2—COOH + NaOH \rightarrow H_2NCH_2—COONa + H_2O$$

With alcohols these acids produce esters:

$$\underset{\text{glycine}}{H_2N—CH_2—COOH} + CH_3OH \rightarrow \underset{\text{glycine methyl ester}}{H_2N—CH_2—COOCH_3} + H_2O$$

Amino acids exhibit their basic nature when they react with acids to produce salts:

$$\underset{\text{glycine}}{H_2N—CH_2—COOH} + HCl \rightarrow \underset{\text{glycine hydrochloride}}{[H_3\overset{+}{N}—CH_2—COOH]Cl^-}$$

Thus, amino acids have amphoteric properties. Two amino acid molecules can react with each other when one functional group of one of them encounters the opposite functional group of the other. The result is that an incomplete amide called dipeptide is formed:

$$HOOC—CH_2—NH_2 + \underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{C}}}—CH_2—NH_2 \xrightarrow{-H_2O}$$

$$\rightarrow \underset{\text{dipeptide of glycine}}{HOOC—CH_2—NH—\overset{\displaystyle O}{\overset{\|}{C}}—CH_2—NH_2}$$

The imide bonding (A) formed in such amides is characteristic of dipeptides and is known as a peptide bond

$$\underset{A}{—NH—\overset{\displaystyle O}{\overset{\|}{C}}—}$$

A dipeptide can react with a new amino acid molecule to yield a tripeptide which can, in turn, react with a fourth amino acid molecule and so on. As a result, the so-called polypeptides are formed. These are the building blocks which the protein molecules are made up of.

Proteins contain more than 25 different amino acids. All proteins differ considerably from one another both in qualitative and quantitative contents of various amino acids and in the arrangement of amino acid residues.

As we already know, amino acids can be bonded both by carboxylic and amino groups to form chains called polypeptides. Protein molecules may consist of one or several polypeptide chains, which may be open, branched or cyclic. An important role in the formation of various polypeptide chains is played by disulphide bridges, —S—S—, which are formed due to sulphur atoms present in certain amino acids such as cystine, and also due to hydrogen bonds between H of NH in one polypeptide unit and O of C=O in another such unit. As a result, aggregates of a large size are formed. Molecular masses of the proteins range, therefore, from tens of thousands to tens of millions.

In an organism, proteins exist in the form of colloids. Only a few parts of an organism such as hair, nails are made up of solid proteins which are commonly known as fibrous proteins. Proteins retain their properties only under definite conditions. At high temperatures they are coagulated and become insoluble. This is known as *denaturation* of proteins.

All proteins are amphoteric in nature. In a neutral solution, the basic (amino) and acidic (carboxylic) groups of proteins are dissociated into ions as in the case of the bipolar ions of amino acids.

An alkaline solution containing copper ions acquires a characteristic violet colouration in the presence of proteins. This is known as *biuret test.*

On heating with nitric acid proteins form bright yellow coagulate. This reaction is called *xanthoprotein test.* These two colour reactions are considered to be qualitative tests for proteins.

Example 1. Name the following amines according to the IUPAC nomenclature:

(a) $CH_3-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$ (b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH-CH_2-CH_3$

(c) $C_2H_5-\underset{\displaystyle C_6H_5}{\underset{|}{N}}-C_2H_5$

Solution. Amine (a) is an aliphatic primary amine. Its IUPAC name is 2-aminobutane, because only one hydro-

gen atom of an ammonia molecule is replaced by a hydrocarbon residue and the names of such amines are derived from the names of the hydrocarbons by adding the prefix 'amino' to them.

Amine (b) is an aliphatic mixed secondary amine. This is ethylisopropylamine, since in this case two hydrogen atoms in an ammonia molecule are replaced by two different hydrocarbon residues.

Amine (c) is a mixed aliphatic-aromatic tertiary amine. It is diethylphenylamine formed by two aliphatic (ethyl) and one aromatic (phenyl) groups.

Example 2. Write the structural formulas for all isomeric amines with a molecular formula C_3H_9N, omitting the cyclic amines. Give names to all of them.

Solution.

(a) $CH_3—CH_2—CH_2—NH_2$

1-aminopropane
(*n*-propylamine)

(b) $CH_3—\underset{\displaystyle NH_2}{\underset{|}{CH}}—CH_3$

2-aminopropane
(*sec*-propylamine)

(c) $CH_3—NH—C_2H_5$

methylethylamine

(d) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{N}}—CH_3$

trimethylamine

Therefore, the amine with the molecular formula C_3H_9N has four isomers.

Example 3. Write the structural formulas for the isomeric amino acids which have a molecular formula $C_4H_9O_2N$. Name each isomer according to the rational and IUPAC nomenclatures.

Solution. The amino acid, $C_4H_9O_2N$, has five isomers:

(a) $CH_3—CH_2—\underset{\displaystyle NH_2}{\underset{|}{CH}}—COOH$

α-aminobutyric acid
(2-aminobutanoic acid)

(b) $CH_3—\underset{\displaystyle NH_2}{\underset{|}{CH}}—CH_2—COOH$

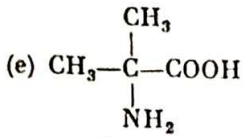
β-aminobutyric acid
(3-aminobutanoic acid)

(c) $\underset{\displaystyle NH_2}{\underset{|}{CH_2}}—CH_2—CH_2—COOH$

γ-aminobutyric acid
(4-aminobutanoic acid)

(d) $\underset{\displaystyle NH_2}{\underset{|}{CH_2}}—\underset{\displaystyle CH_3}{\underset{|}{CH}}—COOH$

α-methyl-β-aminopropionic acid
(2-methyl-3-aminopropanoic acid)



(e) $CH_3-\underset{\displaystyle NH_2}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-COOH$

α-methyl-α-aminopropionic acid
(2-methyl-2-aminopropanoic acid)

Example 4. You have been given three organic compounds, glycerol, aniline and formic acid. Identify each of them with the help of characteristic tests.

Solution. Glycerol and formic acid are readily soluble, while aniline is sparingly soluble in water. So when water is added to the samples, aniline can be isolated. Now, we can carry out characteristic tests for aniline, say, with hydrochloric acid which yields aniline hydrochloride, a salt:

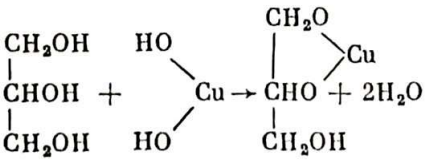
$$C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_2 \cdot HCl$$

The remaining two compounds, glycerol and formic acid, may be identified as follows. These samples are treated with litmus. Only in the acid sample does litmus change its colour to red.

Once we have detected formic acid, we can confirm this by adding H_2SO_4, as a result of which formic acid decomposes to yield carbon monoxide which can, in turn, be detected by passing over copper oxide until the latter is reduced to metallic copper:

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

Finally, to identify glycerol, we add a $Cu(OH)_2$ solution to it: deep-blue solution of copper glycerate is produced



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} HO \\ \diagdown \\ Cu \\ \diagup \\ HO \end{array} \rightarrow \begin{array}{l} CH_2O \\ | \quad \diagdown \\ CHO \quad Cu \\ | \\ CH_2OH \end{array} + 2H_2O$$

Example 5. Combustion of 5.64 g of a compound produced 3.84 g of H_2O and 15.94 g of CO_2. Besides C and H, the compound also contains 15.38% nitrogen. Determine the empirical formula of the compound. Which class of organic compounds does it belong to?

Solution. Let us first determine the mass of hydrogen in the 5.64-g sample:

$$2H_2 + O_2 = 2H_2O$$

2×18 g of H_2O are produced from 4 g of H_2

3.84 g of H_2O are produced from $\frac{4\text{ g} \times 3.84\text{ g}}{2 \times 18\text{ g}} = 0.43$ g of H_2

Next, let us determine the mass of carbon in the same sample:

$$C + O_2 = CO_2$$

44 g of CO_2 are formed from 12 g of C

15.94 g of CO_2 are formed from $\frac{15.94\text{ g} \times 12\text{ g}}{44\text{ g}} = 4.35$ g of C

Hence the sample contains $5.64 - (0.43 + 4.35) = 0.86$ g of nitrogen.

Now we can calculate the ratio of the relative numbers of carbon, hydrogen and nitrogen atoms:

$$C : H : N = \frac{4.35}{12} : \frac{0.43}{1} : \frac{0.86}{14} = 0.38 : 0.43 : 0.06$$

Since a molecule cannot have less than one atom, the above ratio is to be divided by the lowest number. Thus, we get

$$C : H : N = \frac{0.38}{0.06} : \frac{0.43}{0.06} : \frac{0.06}{0.06} = 6 : 7 : 1$$

The empirical formula of the given compound is, therefore, C_6H_7N or $C_6H_5NH_2$. It belongs to an aromatic amine.

Example 6. By reacting 26.5 g of a mixture of aniline, phenol and benzene with bromine, a precipitate was obtained. When the same mixture was treated with sodium hydroxide, 11.6 g of a new substance were produced. By reducing the whole mixture with hydrogen, 8.4 g of a cyclic hydrocarbon were prepared. Determine the mass percent of each component in the original mixture.

Solution. 1. Of the three compounds present in the mixture only phenol reacts with alkali. Therefore, we

can determine the mass of phenol in the mixture:

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

116 g of C_6H_5ONa come from 94 g of C_6H_5OH

11.6 g of C_6H_5ONa come from $\frac{11.6\ g \times 94\ g}{116\ g}$

$= 9.4$ g of C_6H_5OH

2. Of the three compounds, benzene alone is reduced to a cyclic hydrocarbon by hydrogen. So we can calculate the mass of benzene in the mixture:

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$$

84 g of C_6H_{12} come from 78 g of C_6H_6

8.4 g of C_6H_{12} come from $(8.4\ g \times 78\ g)/84\ g =$

$= 7.8$ g of C_6H_6

3. Hence, the mixture contains $26.5 - (7.8 + 9.4) = 9.3$ g of aniline.

4. Mass percent of aniline in the mixture:

26.5 g constitute 100%

9.3 g constitute $(9.3\ g \times 100\%)/26.5\ g = 35.1\%$

5. Mass percent of phenol in the mixture:

26.5 g constitute 100%

9.4 g constitute $(9.4\ g \times 100\%)/26.5\ g = 35.5\%$

6. Mass percent of benzene in the mixture:

26.5 g constitute 100%

7.8 g constitute $(7.8\ g \times 100\%)/26.5\ g = 29.4\%$

Therefore, the given mixture consists of 35.1% aniline, 35.5% phenol and 29.4% benzene.

Example 7. Hydrogen chloride was passed into 50 g of an anhydrous mixture of benzene, aniline and phenol to yield 26 g of a precipitate which was filtered off. The filtrate when treated with a caustic soda solution got separated into two layers. The upper layer occupied a volume of 17.7 ml and had a density of 0.88 g/ml. Find out the mass percent of each component in the mixture.

Solution. 1. Among the three compounds only aniline reacts with hydrogen chloride to yield aniline hydro-

chloride. So we can calculate the mass of aniline in the mixture:

$$C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_2 \cdot HCl$$

129.5 g of $C_6H_5NH_2 \cdot HCl$ come from 93 g of $C_6H_5NH_2$

26 g of $C_6H_5NH_2 \cdot HCl$ come from $\frac{26\ g \times 93\ g}{129.5\ g} =$

$= 18.67$ g of aniline

Therefore, the mass percent of aniline:

50 g of the mixture constitute 100%

18.67 g of $C_6H_5NH_2$ constitute $\frac{18.67\ g \times 100\%}{50\ g} = 37.35\%$

2. On treating the filtrate with sodium hydroxide two layers are formed. The lower layer consists of sodium phenolate formed following the equation: $C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$, while the upper layer is of benzene. According to the specified conditions, benzene occupies a volume of 17.7 ml. Hence, its mass is 17.7 ml × 0.88 g/ml = 15.576 g. On conversion to mass percent:

50 g of the mixture constitute 100%

15.576 g of C_6H_6 constitute $\frac{15.576\ g \times 100\%}{50\ g} = 31.15\%$

The remaining mass of 50 — (15.576 + 18.67) = 15.75 g is due to phenol. In terms of mass percent we get:

50 g of the mixture constitute 100%

15.75 g of C_6H_5OH constitute $\frac{15.75\ g \times 100\%}{50\ g} = 31.5\%$

Thus, the given mixture consists of 37.35% $C_6H_5NH_2$, 31.15% C_6H_6 and 31.5% C_6H_5OH.

PROBLEMS AND EXERCISES

1. Which compounds are called amines? How are they classified? What class of compounds does aniline belong to?

2. How will you account for the similar properties of amines and ammonia?

3. How does the mutual effect of atoms in aniline molecules manifest itself?

4. Name the primary amines displayed below:

(a) $CH_3-CH_2-CH_2-NH_2$

(b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-NH_2$

(c) $CH_3-\overset{\displaystyle NH_2}{\overset{|}{CH}}-CH_3$

(d) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-NH_2$

5. Name the following secondary amines:

(a) $CH_3-CH_2-NH-CH_3$

(b) $C_6H_5NHCH_3$

(c) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH-CH_3$

(d) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH-CH_2-CH_3$

6. Name the following tertiary amines:

(a) $C_3H_7N-\underset{\displaystyle C_3H_7}{\underset{|}{C_3H_7}}$

(b) $C_2H_5-\underset{\displaystyle CH_3}{\underset{|}{N}}-C_2H_5$

(c) $C_6H_5N(CH_3)_2$

(d) $(C_6H_5)_2NCH_3$

7. State whether amines are basic, acidic or amphoteric in nature.

8. Who was the first to convert nitro compounds into amines and when this was carried out? Which material was then used as a reductant?

9. Which compounds are termed as amino acids? How do the functional groups in amino acids manifest themselves in chemical reactions?

10. State whether amino acid solutions will be acidic, basic or neutral to indicators.

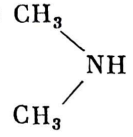
11. State the difference and the similarity between the amphoteric properties of amino acids and metal hydroxides.

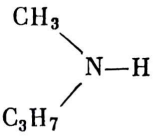
12. Which of the following compounds will react with aminoacetic acid: $Ba(OH)_2$, C_2H_5OH, HCl?

13. Which chemical compounds are used in an organism for synthesizing proteins?

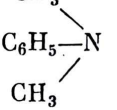
14. Which colour tests are qualitative for proteins? What do you mean by denaturation of protein?

15. Name the amines displayed below:

(a) 

(b) 

(c) $C_6H_5—NH—C_2H_5$

(d) 

16. Write the structural formulas for the following amines: (a) dimethylethylamine, (b) ethylpropylamine, (c) N,N-dimethylaniline, and (d) diphenylamine.

17. Write down the structural formulas for the isomeric amines with a molecular formula $C_4H_{11}N$, (omitting the cyclic amines) and name each of them.

18. Write down the equations for the reactions that take place when aniline, ammonia and methylamine react separately with hydrochloric acid. Which general properties do these compounds exhibit?

19. Write down the equation to represent the reduction of nitrobenzene to aniline with the aid of ammonium sulphide (a reaction discovered and developed by N.N. Zinin).

20. What mass of aniline was obtained when hydrogen gas produced by reacting iron with a volume of 200 ml of 0.5 *M* hydrochloric acid solution was passed into a nitrobenzene solution?

21. Why are aromatic amines less basic as compared to aliphatic amines? Write down a chemical equation to prove that aniline is basic in nature.

22. Write down the equations to represent the reactions which may help carry out the following conversions:

$$CH_4 \rightarrow C_2H_2 \rightarrow C_6H_6 \rightarrow C_6H_5NO_2 \rightarrow C_6H_5NH_2$$

23. How many grams of aniline are needed to neutralize 7.7 ml of a hydrochloric acid solution which has a density of 1.19 g/ml and contains 40% by mass of HCl?

24*. 26.5 g of a mixture of aniline, phenol and benzene reacted with bromine to yield 122 g of a precipitate. When the same mixture was treated with sodium hydroxide, 11.6 g of a new compound were produced. By re-

ducing the whole mixture with hydrogen, 8.4 g of a cyclic hydrocarbon were obtained. Determine the mass percent of each component in the mixture.

25*. A 90%-yield of a mononitro derivative of benzene was produced when 0.2 mole of benzene was nitrated with a mixture of concentrated nitric and sulphuric acids at 50-60 °C. How many millilitres of an amine of density 1.022 g/ml would be formed, if this nitro derivative was reduced with iron in dilute hydrochloric acid, the yield of the amine produced by reduction being 75%?

26*. 16.6 g of a mixture of ethyl and propyl alcohols when treated with an excess sodium liberated 3.36 litres of hydrogen at STP. What is the composition of the original mixture of alcohols? What mass of this mixture will be required so that the evolved gas can reduce 24.6 g of nitrobenzene to the respective amine?

27. Write the structural formulas for the following amino acids: (a) β-aminobutyric acid, (b) β,δ-diaminovaleric acid, (c) α,γ-diaminoisocaproic acid and (d) β,ε-diaminocaproic acid.

28. Name the following amino acids according to the rational nomenclature:

(a) $CH_2(NH_2)-CH_2-COOH$

(b) $CH_3-CH(NH_2)-CH_2-CH(NH_2)-COOH$

(c) $CH_3-CH(CH_3)-CH(NH_2)-COOH$

(d) $CH_3-CH(NH_2)-CH(NH_2)-COOH$

29. Write the structural formulas for the isomeric amino acids corresponding to a molecular formula $C_3H_7O_2N$. Name each of them according to the rational and IUPAC nomenclatures.

30. Prepare aminoacetic acid from ethyl alcohol and employing suitable inorganic compounds only.

31. Write down the equations to represent the reactions which may help bring about the following conversions:

(a) $CH_4 \rightarrow CH_3Cl \rightarrow C_2H_6 \rightarrow CH_3COH \rightarrow CH_3COOH \rightarrow$
$\rightarrow CH_2Cl \rightarrow COOH \rightarrow CH_2NH_2-COOH$

(b) $CH_4 \rightarrow C_3H_8 \rightarrow CH_2NH_2-CH_2-COOH$

32. What volume of ammonia will be required to convert 27.8 g of bromoacetic acid into glycine, if it is known that the loss of ammonia is 5%?

33. Write down the equations for the reactions which prove that amino acids are amphoteric in nature. Why do amino acids not change the colour of the litmus indicator?

34. How are dipeptides formed? Write down the equation to represent the reaction that takes place between α-aminoacetic and α-aminopropionic acids.

9
TEST YOUR KNOWLEDGE

9.1 INORGANIC CHEMISTRY

Task 1

1. Write down the molecular and the ionic equations to represent the reactions which may help bring about the following transformations:

$$Fe \rightarrow Fe_2(SO_4)_3 \rightarrow FeCl_3 \rightarrow Fe(NO_3)_3 \rightarrow Fe_2O_3$$

For the redox reactions indicate the oxidants and reductants.

2. Which of the following salts can be hydrolyzed: $CuSO_4$, K_2SO_4 and Na_2S? Write down the complete and net ionic equations for the hydrolysis of each salt wherever possible.

3. Determine the molarity of an orthophosphoric acid solution 250 ml of which contain 4.9 g of orthophosphoric acid.

Task 2

1. Write the equations in molecular and ionic forms to represent the reactions that may help bring about the following conversions:

$$Al \rightarrow NaAlO_2 \rightarrow Al(OH)_3 \rightarrow Al_2(SO_4)_3 \rightarrow AlCl_3$$

Indicate the oxidants and the reductants in the case of redox reactions.

2. Among the salts, $CaCO_3$, Na_2CO_3 and K_2SiO_3, find out those which can be hydrolyzed and write the complete and net ionic equations for their hydrolysis.

3. How many millilitres of 30% H_2SO_4 solution (density 1.2 g/ml) are to be used in order to prepare 500 ml of 10% H_2SO_4 solution (density 1.04 g/ml)?

Task 3

1. Write down the molecular and the ionic equations for the reactions involved in the following transformations:

$$Cr \rightarrow Cr_2(SO_4)_3 \rightarrow Cr(NO_3)_3 \rightarrow KCrO_2 \rightarrow Cr(OH)_3$$

Point out the oxidizing and reducing agents in the case of redox reactions.

2. Which of the following salts undergo hydrolysis: KNO_3, $NaNO_2$ and $Fe_2(SO_4)_3$? Express these hydrolysis reactions in the form of complete and net ionic equations.

3. How many millilitres of water are to be added to 300 ml of a 20% solution of an acid whose density is 1.14 g/ml in order to get a solution containing 15% by mass of the acid?

Task 4

1. Write down the equations in the molecular and ionic forms to represent the reactions required to bring about the following conversions:

$$Cu \rightarrow CuSO_4 \rightarrow Cu(OH)_2 \rightarrow Cu(NO_3)_2 \rightarrow NO_2$$

Indicate the oxidants and the reductants in the case of redox reactions.

2. Among the salts, $Ca(NO_3)_2$, K_2SO_3 and Na_3PO_4, indicate those which can be hydrolyzed. Write down the complete and net ionic equations for the hydrolysis.

3. How many grams of potassium carbonate are there in 250 ml of 0.2 *M* solution?

Task 5

1. Write down the equations in the molecular and ionic forms for the reactions involved in the following conversions:

$$Ca \rightarrow Ca(NO_3)_2 \rightarrow CaCO_3 \rightarrow CO_2 \rightarrow Ca(HCO_3)_2$$

Indicate the oxidants and the reductants for the redox reactions.

2. Which of the following salts undergo hydrolysis: Na_2SO_4, $CuCl_2$ and K_2S? Write down the complete and net ionic equations for their hydrolysis.

3. 200 g of 20% $CuCl_2$ solution were evaporated to a mass of 120 g. What is the percent strength of the final solution?

Task 6

1. Write the molecular and ionic equations to represent the reactions which may help bring about the follow-

ing conversions:

$$K \rightarrow KOH \rightarrow K_2CO_3 \rightarrow KNO_3 \rightarrow KNO_2$$

Point out the oxidants and the reductants for the redox reactions.

2. Which of the following salts can be hydrolyzed: Na_2SiO_3, $Ca(NO_2)_2$ and KCl? Write down the complete and net ionic equations for their hydrolysis.

3. If 40 g of a salt are dissolved in 460 ml of water, what will be the mass percent of the solute in the solution?

Task 7

1. Employing the ion-electron method, balance the following chemical equation:

$$Hg + HNO_3(conc.) \rightarrow Hg(NO_3)_2 + NO_2 + H_2O$$

For this redox reaction point out the oxidation and the reduction processes, and also the oxidizing and the reducing agents in the half-reactions.

2. Write down the molecular and ionic equations to represent the reactions which bring about the following conversions:

$$CuO \rightarrow Cu(NO_3)_2 \rightarrow Cu(OH)NO_3 \rightarrow Cu(NO_3)_2 \rightarrow Cu(OH)_2 \rightarrow CuO$$

3. 800 g of 5% H_3PO_4 solution were added to 200 g of 10% H_3PO_4 solution. Determine the percent strength of the final solution.

Task 8

1. Making use of the ion-electron method, balance the following equation:

$$MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + H_2O$$

Indicate the oxidation and reduction processes, and also the oxidant and the reductant.

2. Write down the molecular and ionic equations for the reactions which may be used to bring about the following conversions:

$$FeO \rightarrow FeCl_2 \rightarrow Fe(OH)_2 \rightarrow FeSO_4 \rightarrow Fe(NO_3)_2 \rightarrow FeO$$

3. A volume of 2 litres of a solution contains 32 g of $CuSO_4$. Determine the molar concentration of the solution.

Task 9

1. Using the ion-electron method, balance the following equation:

$$Zn + H_2SO_4 \xrightarrow{t} ZnSO_4 + H_2S + H_2O$$

In the two half-reactions show the oxidation and reduction processes, and also the oxidant and the reductant.

2. Write down the molecular and ionic equations for the reactions involved in the following transformations:

$$Na_2O \rightarrow NaOH \rightarrow Na_2SiO_3 \rightarrow Na_2CO_3 \rightarrow NaHCO_3$$

3. How many grams of sodium chloride are required to prepare 300 g of 10% NaCl solution?

Task 10

1. Employing the ion-electron method, balance the following chemical equation:

$$KMnO_4 + HCl \rightarrow MnCl_2 + Cl_2 + KCl + H_2O$$

In the half-reactions show the oxidation and the reduction processes, and also the oxidant and the reductant.

2. Write the chemical equations in the molecular and ionic forms to represent the reactions that occur when the following transformations are carried out:

$$Zn \rightarrow ZnCl_2 \rightarrow Zn(OH)_2 \begin{cases} \rightarrow Na_2ZnO_2 \\ \rightarrow Zn(NO_3)_2 \end{cases} \rightarrow Zn(OH)_2$$

3. How many grams of potassium sulphate are required in order to prepare 200 ml of 0.5 *M* solution of K_2SO_4?

Task 11

1. Make use of the ion-electron method to balance the following chemical equation:

$$Pb + HNO_3(dil.) \rightarrow Pb(NO_3)_2 + NO + H_2O$$

In the half-reactions indicate the oxidation and reduction processes, and also the oxidant and the reductant.

2. Write the molecular and ionic equations for the reactions that take place when the conversions shown below are carried out:

$$Ca \rightarrow Ca(OH)_2 \rightarrow CaCO_3 \rightarrow CO_2 \rightarrow Ca(HCO_3)_2$$

3. Calculate the mass percent of sodium hydroxide in its aqueous solution, 120 g of which contain 3 moles of NaOH.

Task 12

1. Use the ion-electron method to balance the following chemical equation:

$$K_2Cr_2O_7 + HCl \rightarrow CrCl_3 + Cl_2 + KCl + H_2O$$

Indicate in the half-reactions the oxidation and reduction processes, and also the oxidizing and the reducing agents.

2. Write down the molecular and ionic equations for the reactions that occur when the following conversions are brought about:

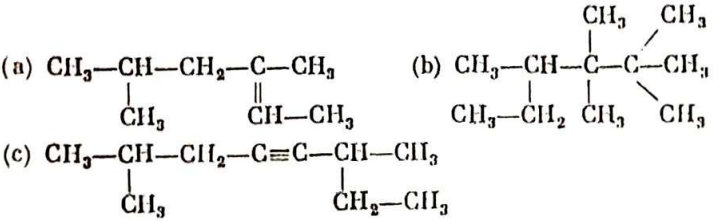
$$MgO \rightarrow Mg(NO_3)_2 \rightarrow MgCO_3 \rightarrow CO_2 \rightarrow Mg(HCO_3)_2 \rightarrow MgCO_3$$

3. How many millilitres of water should be added to 50 g of a nitric acid solution containing 30% by mass of HNO_3 in order to get a solution containing 10% by mass of HNO_3?

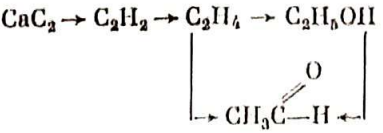
9.2 ORGANIC CHEMISTRY

Task 1

1. Name the following hydrocarbons by the rational and IUPAC nomenclatures:



2. Write down the equations to represent the reactions involved in the following conversions:



3. A mass of 50 g of ethyl alcohol was mixed with concentrated sulphuric acid and heated to 160°C. The

yield of the obtained ethylene was found to be 89% of the theoretical amount. How many litres of ethylene were collected?

Task 2

1. Which hydrocarbons are obtained when a mixture of phenyl chloride and isopropyl chloride is treated with metallic sodium? Name the hydrocarbons thus obtained.
2. Write down the equations for reactions which can help bring about the following transformations:

$$C_2H_6 \rightarrow C_2H_4 \rightarrow CH_3COH \rightarrow CH_3COOH \rightarrow CH_3COOC_2H_5$$

3. 160 g of bromobenzene were obtained when 156 g of benzene were brominated in the presence of a catalyst. Calculate the yield of bromobenzene (in %) of the theoretical amount.

Task 3

1. Write the structural formulas for the following compounds:
(a) 3-ethyl-2-methylbenzene, (b) 2,2,4,4-tetramethylpentane,
(c) 2-methyl-1,3-butadiene, (d) 2,2-dimethylpropanoic acid.
2. Write down the equations to represent the reactions which are required for carrying out the following conversions:

$$C_2H_2 \rightarrow C_6H_6 \rightarrow C_6H_5NO_2 \rightarrow C_6H_5NH_2$$

3. Calculate the mass of *o*-bromotoluene obtained when 1 ton of toluene is brominated in the presence of a catalyst. The yield of the product is 30% of the theoretical amount.

Task 4

1. Write down the structural formulas for the following hydrocarbons: (a) dimethylisobutylethylene (consider 2 cases), (b) methylisopropyl-*tert*-butylmethane, (c) isopropyl-*sec*-butylacetylene, (d) *m*-ethylpropylbenzene.

2. Write the equations for the reactions involved in the following transformations:

$$CH_3COH \rightarrow CH_3COOH \rightarrow CH_2Cl—COOH \rightarrow CH_2NH_2—COOH$$

3. What volume of hydrogen gas will be evolved when 4 g of ethylene glycol are reacted with 2.3 g of metallic sodium?

Task 5

1. Write down the structural formulas for the following compounds: (a) 2,4-dimethylpentanal, (b) 2,3-dimethyl-2-butanol, (c) propyl propionate, (d) ethylpropylamine.

2. Write down the equations for the reactions that occur when the following transformations are carried out:

$$C \rightarrow CH_4 \rightarrow C_3H_8 \rightarrow CH_2NH_2—CH_2COOH$$

3. Determine the mass percent of 1-hexene in a mixture, knowing that a mass of 5 g of such a mixture add a mass of 8 g of bromine.

Task 6

1. Write the structural formulas for the following compounds: (a) β-aminobutyric acid, (b) N,N-dimethylaniline, (c) 2,2,3-trimethylpentanal, (d) 2,3-dimethyl-2-butanol.

2. Write the chemical equations to represent the reactions that take place when the following transformations are carried out:

$$C_2H_4 \rightarrow C_2H_6 \rightarrow C_2H_5Cl \rightarrow C_2H_5OH \rightarrow CH_3COOCH_3$$

3. What volume of acetylene is required at standard conditions in order to prepare 300 g of acetic acid? The yield of acetic acid is 90% of the theoretically possible amount.

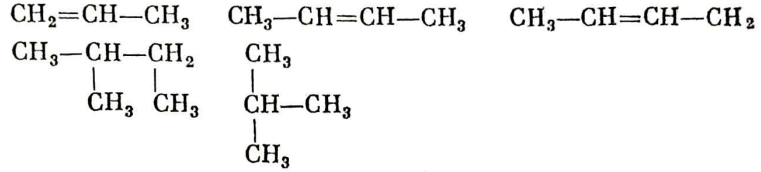
Task 7

1. Write down the structural formulas for the following hydrocarbons? (a) 2,3-dimethyl-1-pentene, (b) 3-ethyl-3-methylhexane.

2. Write the equations for the reactions which may help bring about the following conversions:

$$CaC_2 \rightarrow C_2H_2 \rightarrow C_6H_6 \rightarrow C_6H_5NO_2$$
$$\downarrow$$
$$C_6H_5Br$$

3. Name the following compounds:



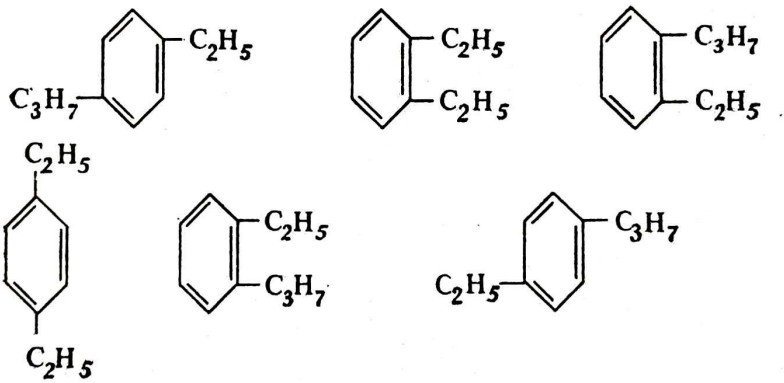
Task 8

1. Write the structural formulas of the following hydrocarbons: (a) 2-ethyl-2-methylbutane, (b) 2,3-dimethyl-1-hexene.

2. Write down the equations to represent the reactions which take place when the following transformations are brought about:

$$CH_4 \rightarrow CH_3Cl \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_5Cl$$

3. Name the compounds displayed below:



4. A mass of 120 kg of technical-grade calcium carbide was treated with water to liberate 33.6 m^3 of a gas. Determine the mass percent of pure calcium carbide in the technical-grade sample.

Task 9

1. Write down the structural formulas for the following hydrocarbons: (a) 2,3-dimethyl-2-hexene, (b) 2-methyl-1,3-butadiene.

2. Write the equations (in the structural form) for the reactions which occur when the following conversions

are carried out:

$$CH_4 \rightarrow C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_4Br_2 \rightarrow C_2H_4(OH)_2$$

3. Classify the following compounds and name them:

(a) $CH_3—CH_2—O—CH_3$

(b) $CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—OH$

(c) $CH_2OH—CHOH—CH_3$

(e) $CH_2OH—CHOH—CH_2OH$

(d) $CH_2OH—CH_2—CH_2OH$

(g) $CH_3—CH_2—CH_2—OH$

(f) $CH_3—CHOH—CH_3$

4. How many grams of ethyl acetate may be prepared from 60 g of acetic acid and the necessary amount of alcohol, if the practical yield is 90%.

Task 10

1. Write the structural formulas for the following compounds: (a) 2-methyl-2-propanol and (b) 2,2-dimethylpropane.

2. Write the equations (in the structural form) for the reactions which may help bring about the following conversions:

$$CH_4 \rightarrow CH_3Br \rightarrow CH_3OH \rightarrow H—\overset{\displaystyle O}{\overset{\|}{C}}—H \rightarrow H—\overset{\displaystyle O}{\overset{\|}{C}}—OH$$

3. Classify the following compounds and name them:

(a) $CH_3—CH{=}CH—CH_3$

(b) $C_2H_4(OH)_2$

(c) CH_2Cl_2

(d) $C_3H_5(OH)_3$

(e) $C_{17}H_{34}$

(f) CH_3OH

(g) C_8H_{18}

(h) $CH_3—CH_2—CH_2—CH_3$

4. What volume of hydrogen will be evolved at standard conditions when 8 g of magnesium are treated with acetic acid?

Task 11

1. Write down the structural formulas for the following compounds: (a) 2,2-dimethylbutanal and (b) 2,3-dimethyl-3-hexene.

2. Write down the equations for the reactions which take place when the following transformations are carried

out:

$$C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow C_6H_6 \rightarrow C_6H_5Cl$$

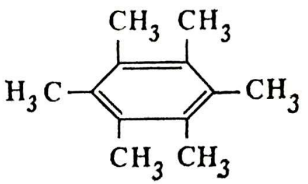
3. Classify the following compounds:

(a) $CH{\equiv}C{-}CH_2{-}CH_3$ (b) $CH_3{-}C{\equiv}C{-}CH{=}CH{-}CH_3$

(c) $C_6H_5{-}C_2H_5$ (d) $CH{\equiv}C{-}CH_3$

(e) C_6H_{14} (f) C_7H_{14}

(g)



4. An excess solution of sodium hydroxide was added to 200 g of a phenol solution containing 10% by mass of C_6H_5OH. How many grams of sodium phenolate were formed?

Task 12

1. Write down the structural formulas for the following compounds: (a) 2-methylbutanoic acid, and (b) 4,4-dimethyl-2-pentyne.

2. Write down the chemical equations to represent the reactions that occur in the following conversions:

$$C \rightarrow CH_4 \rightarrow CH_3Cl \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_5OH$$

3. How many different alcohols are displayed below? Name them.

(a) $CH_3{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$ (b) $C_2H_5{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}C_2H_5$

(c) $C_2H_5{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}{-}CH_3$ (d) $CH_3{-}\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2{-}CH_3$

(e) $HO{-}CH_2{-}\underset{\displaystyle CH_2}{\underset{|}{CH_2}}{-}\underset{\displaystyle CH_3}{\underset{|}{CH_2}}$ (f) $CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}CH_3$

4. What volume of oxygen will be needed for a complete combustion of 10 litres of acetylene containing 10% impurities?

APPENDIX

Table I. Solubility of Acids, Bases and Salts in Water

Cations																				Anions
H^+	K^+	Na^+	NH_4^+	Ba^{2+}	Ca^{2+}	Mg^{2+}	Al^{3+}	Cr^{3+}	Fe^{2+}	Fe^{3+}	Ni^{2+}	Co^{2+}	Mn^{2+}	Zn^{2+}	Ag^+	Hg^+	Hg^{2+}	Pb^{2+}	Sn^{2+}	Cu^{2+}	
	sol	sol	sol ↑	sol	spar	ins	ins	ins	ins	ins	ins	ins	ins	ins	x	x	x	ins	ins	ins	OH^-
sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	ins	ins	sol	SPAR	sol	sol	Cl^-
sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	ins	ins	ins	SPAR	sol	sol	Br^-
sol ↑	sol	sol	sol	—	—	—	—	—	ins	ins	ins	ins	ins	ins	ins	ins	spar	INS	spar	x	I^-
sol ↑	sol	sol	sol	ins	ins	ins	x	x	ins	x	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	S^{2-}
sol	sol	sol	sol	ins	spar	sol	sol	sol	sol	sol	sol	sol	sol	sol	spar	spar	—	ins	x	x	SO_3^{2-}
sol	sol	sol	sol	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	ins	sol	sol	SO_4^{2-}
sol ↑	sol	sol	sol	ins	ins	ins	x	x	ins	x	ins	ins	ins	ins	ins	ins	x	ins	ins	ins	PO_4^{3-}
ins	sol	sol	x	ins	ins	—	—	—	—	—	—	—	—	—	x	x	x	—	—	—	CO_3^{2-}
sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	sol	—	sol	SiO_3^{2-}
																					NO_3^-

Note: sol stands for soluble substances (more than 1 g in 100 g of water), spar for sparingly soluble substances (from 0.01 to 1 g in 100 g of water), ins for practically insoluble compounds (less than 0.01 g in 100 g of water), — stands for a substance which exists, but cannot be prepared in aqueous media by exchange reactions, x means that the compound does not exist, ↑ points out that the substance is liberated as a gas or decomposes to give off a gas, SPAR and INS show that the solubilities of the respective compounds increase to a great extent in hot water.

Table II. Relative Molecular Masses of Inorganic Compounds*

	39.0	23.0	137.0	40.0	24.0	27.0	52.0	56.0	56.0	55.0	65.0	108.0	201.0	201.0	64.0	207.0	209.0	119.0	1.0	18.0
	K^+	Na^+	Ba^{2+}	Ca^{2+}	Mg^{2+}	Al^{3+}	Cr^{3+}	Fe^{2+}	Fe^{3+}	Mn^{2+}	Zn^{2+}	Ag^+	Hg^{2+}	Hg^+	Cu^{2+}	Pb^{2+}	Bi^{3+}	Sn^{2+}	H^+	NH_4^+
17.0 OH^-	56	40	171	74	58	78	103	90	107	89	99	125	235	218	98	214	260	153	18	35
35.5 Cl^-	74.5	58.5	208	111	95	133.5	158.5	127	162.5	126	136	143.5	272	236.5	135	278	315.5	190	36.5	53.5
32.0 S^{2-}	110	78	169	72	56	150	200	88	208	87	97	248	233	434	96	239	514	151	34	68
127.0 I^-	166	150	391	294	278	408	433	310	437	309	319	235	455	328	318	461	590	373	128	145
80.0 Br^-	119	103	297	200	184	267	292	216	296	215	225	188	361	281	224	367	449	279	81	98
80.0 SO_3^{2-}	158	126	217	120	104	294	344	136	352	135	145	296	281	482	144	287	658	199	82	116
96.0 SO_4^{2-}	174	142	233	136	120	342	392	152	400	151	161	312	297	498	160	303	706	215	98	132
95.0 PO_4^{3-}	212	164	601	310	262	122	147	358	151	355	385	419	793	698	382	811	304	547	98	149
60.0 CO_3^{2-}	138	106	197	100	84	234	284	116	292	115	125	276	261	462	124	267	598	179	62	96
76.0 SiO_3^{2-}	154	122	213	116	100	282	332	132	340	131	141	292	277	478	140	283	646	195	78	112
62.0 NO_3^-	101	85	261	164	148	213	238	180	242	179	189	170	325	263	188	331	395	243	63	80
59.0 $H_2C_2O_2^-$	98	82	255	158	142	204	229	174	233	173	183	167	319	260	182	325	386	237	60	77
16.0 O^{2-}	94	62	153	56	40	102	152	72	160	71	81	232	217	418	80	223	466	135	—	—

* Rounded values.

Table III. Relative Molecular Masses of a Few Organic Compounds *

			$-CH_3$ 15	$-C_2H_5$ 29	$-C_3H_7$ 43	$-C_4H_9$ 57	$-C_6H_6$ 77	$-C_{17}H_{35}$ 239	$CH_2-CH-CH_2$ 41	$-CH_2NH_2$ 30	$-C_2H_4NH_2$ 44
Aliphatic hydrocarbons											
(a) saturated	H—	1	16	30	44	8					
(b) ethylenic	$CH_2=CH-$	27	42	56	70	84	104				
(c) acetylenic	$CH\equiv C-$	25	40	54	68	82	102				
Halohydrocarbons	Cl^-	35.5	50.5	64.5	78.5	92.5	112.5				
	Br^-	80	95	109	123	137	157				
	I^-	127	142	156	170	184	204				
Aromatic hydrocarbons	$-C_6H_5$	77	92	106	120	134	154				
Alcohols and phenols	—OH	17	32	46	60	74	94		92		
Ethers	C_2H_5-O-	45	60	74	88	102	122				
Aldehydes	$-C(=O)H$	29	44	58	72	6	106				
Carboxylic acids	$-C(=O)OH$	45	60	74	88	102	122	284		75	89
Esters	$-C(=O)-O-CH_3$	59	74	88	102	116					
	$-C(=O)-O-C_2H_5$	73	88	102	116	130					
Nitrocompounds	$-NO_2$	46					123				
Primary amines	$-NH_2$	16	31	45	59	73	93				
Sulphonic acids	$-SO_3H$	81					158				

* Rounded values.

Table IV. Degrees of Dissociation of Acids, Bases and Salts in 0.1 *N* Aqueous Solutions at 18°C

Electrolyte	Formula	Degree of dissociation
	Acids	
Nitric	HNO_3	92
Hydrochloric	HCl	91
Hydrobromic	HBr	90
Hydroiodic	HI	90
Sulphuric	H_2SO_4	58
Oxalic	$H_2C_2O_4$	31
Phosphoric	H_3PO_4	26
Sulphurous	H_2SO_3	20
Hydrofluoric	HF	15
Tartaric	$H_2C_4H_4O_6$	13
Acetic	HCH_3COO	1.3
Carbonic	H_2CO_3	0.17
Hydrogen sulphide	H_2S	0.07
Boric	H_3BO_3	0.01
Hydrocyanic	HCN	0.007
	Bases	
Potassium hydroxide	KOH	89
Sodium hydroxide	NaOH	84
Ammonium hydroxide	NH_4OH	1.3
	Salts	
Type M^+A^-	KCl, $NaNO_3$	86
Type $M_2^+A^{2-}$ or $M^{2+}A_2^-$	K_2SO_4, $BaCl_2$	73
Type $M_3^+A^{3-}$ or $M^{3+}A_3^-$	$K_3[Fe(CN)_6]$, $AlCl_3$	65
Type $M^{2+}A^{2-}$	$CuSO_4$	40

Note. 1. The values for strong electrolytes listed above represent apparent degrees of dissociation determined by measuring electrical conductivity of their solutions. 2. In the case of di- and polybasic acids the presented values refer to the first step of their dissociation.

ANSWERS TO PROBLEMS

Sec. 1.1.

19. 0.05 mole, 5 moles, 1 mole. **20.** 6.02×10^{24}, 6.02×10^{26}, 6.02×10^{25}. **26.** 1.25 kg, 0.178 kg, 2.857 kg. **30.** 7.4 g. **33.** $2.69 \times \times 10^{25}$ molecules, 44.64 moles. **34.** 6.49×10^{-23} g, $26.54 \times \times 10^{-23}$ g, 2.99×10^{-23} g, 9.71×10^{-23} g. **36.** 1.204×10^{24} atoms, 1.806×10^{24} atoms, 1.204×10^{24} atoms. **37.** 0.27×10^{23} mole-

cules. 38. 37.21 litres. 40. 1.6×10^{23} atoms of chlorine, $2.15 \times \times 10^{23}$ atoms of nitrogen, 1.34 times as great of nitrogen atoms. 42. 3.7 times. 44. 4 moles. 46. 28. 47. 3.36 litres. 51. $1.204 \times \times 10^{24}$ atoms.

Sec. 1.2

17. 560.4 kg. 18. 2 moles, 3 moles, 0.5 mole. 21. $Na_2S_2O_3$. 23. 15.9. 24. 8. 25. 12. 26. 12. 28. 12. 31. 5, 10, 12. 33. Sn. 37. 72.7%. 38. Potassium. 42. 1.2 g, 135.6 g. 47. 8.77 g. 49. 7.46 litres of CO_2, 3.74 litres of excess O_2. 50. 1.12 litres. 51. 11.2 litres, 44.8 litres, 224 m^3. 52. 88.6×10^3 litres. 53. 13.3%. 54. 168 litres of CO and 840 litres of O_2. 55. C_3H_6, C_4H_8, C_6H_{12}, C_7H_{14}. 59. 103.6, 51.8. 62. 32.6. 63. 1.5 moles. 65. 0.2 g of H_2SO_4.

Sec. 1.3

33. Tellurium. 34. Gallium. 35. Sulphur. 36. Calcium. 40. $A_r = 32$. 41. $A_r = 31$. 42. $A_r = 27$. 43. $A_r = 54$. 44. $A_r = 24$. 45. $A_r = 40$.

Sec. 2.4

1. 6.25%. 2. 21.8 g. 3. 50 g. 4. 28%. 5. 1.75%. 6. 24.5% 7. 3.33%. 8. 28.3 ml. 9. 3.9%. 10. 80.4%. 11. 564.1 litres, 38 litres. 12. 1 kg. 13. 0.5 kg. 14. 360 ml. 15. 70 ml. 16. 5.56 ml. 17. 0.2 *M*. 18. 2.12 kg. 19. 40.9 ml. 20. 41.6 ml of H_2O need be added. 21. 2 ml. 22. 0.0415 *M*. 23. 1.78%. 24. 35.7 ml, 31.3%. 25. 0.025 *M*. 26. 9.2 ml. 27. 80%, 16980 g. 28. 0.05 *M*. 29. 150 g. 30. 36%. 31. 8%. 32. 555 g of $CaCl_2 \cdot 6H_2O$ and 145 ml of H_2O. 33. 113.4 g. 34. 34.78 g. 35. 7.89 g. 36. 85.04 g. 38. 154 ml. 39. 220 ml. 40. 5.16 litres. 41. 1.61 g. 42. 183.1 litres. 43. 2.52 g. 44. 0.5 *M*. 45. 0.1 *M*. 46. 0.5 litre. 47. 2.18 *M*. 48. 7.37%. 49. 9.1 g. 50. 12.4 *M*. 51. 300 ml. 52. 0.8 *M*. 53. 7.9 *M*.

Sec. 2.7

42. 2.8 g. 43. 11.2 litres. 44. 160 g. 45. 0.5 mole. 46. 1 mole. 48. 8 g. 49. 8 g. 50. 0.2 g. 51. 17.9 litres. 52. 1.8 g of HCl were used. Composition: 0.5 g of Cu and 2 g of CuO. 53. Fe. 54. 3 moles. 55. 90%. 56. 31.5 g. 57. 0.4 mole of NH_3 and 0.2 mole of H_2SO_4. 58. 219 g. 59. 56 g. 60. 0.04 mole, 384 g. 61. 9.93 g. 62. 0.08 mole of $Fe(OH)_3$ was produced and 13 g of $FeCl_3$ remained unreacted. 63. 11.2 litres. 64. 40 g.

Sec. 3.1

24. Mg_3N_2. 25. 36.1%. 27. 0.14 litre. 28. 14.4 *M*. 29. 12%. 30. 53.2 ml. 42. 70.7 g. 43. 330 litres of CO_2 and 110 litres of N_2. 44. 7.1 g. 45. 53.97 kg. 47 9.25% KNO_3, 7.78% KNO_2 and 17.2% KOH. 48. 49.47 ml. 49. 25.4%. 50. 2.25% NH_3 and 0.234 g of $Fe(OH)_3$. 51. 35 ml of solution, 8 g of Cu. 52. 5.6 litres of H_2S,

37% CuS and 63% PbS. 53. 0.448 litre of NO, 22.5 ml of HNO_3, 96% Cu. 54. 26.62% H_3PO_4, composition: $(NH_4)_2HPO_4$. 55. 50% NH_3 gas, 0.37% NH_3 solution. 57. 21.25 g. 59. 24.08×10^{21}. 60. 10 moles, 6.02×10^{24} molecules. 61. 0.5 mole, 15 g. 62. 12.3%, 2.06 M. 63. 448 litres, 33.6 litres. 64. 625 litres of O_2. 66. 5.35 g of NH_3 gas remained excess. 67. 28.4 kg. 68. 89.6 litres. 69. 70.6%. 70. 90%. 71. NH_4Cl, 0.3 mole. 72. 61.2 g. 73. 183.75 kg. 74. (a) 140 g, (b) 240 g. 75. 4.13 g of K_2CO_3 and 2.12 g of Na_2CO_3. 76. 82.9 kg. 77. 690 kg. 78. 1.24 kg, 1.04 kg. 79. 3.8 litres. 80. 13.65 m^3, 76.75 kg.

Sec. 3.2

13. 31. 14. P_4O_6. 15. 5 kg, 0.97 kg, 2.9 kg. 20. 0.4% $Ca(H_2PO_4)_2$. 21. 77.6%. 22. 30.5%. 23. 18.5 g. 24. 33.75% Cu, 50% Ca and 16.25% Zn. 25. 19 g. 26. 677 kg of phosphorite, 280 litres of H_2SO_4. 27. 51.9% NaH_2PO_4. 28. 64.7% KH_2PO_4. 29.1 3.2 g of $(NH_4)_2HPO_4$. 41. 39%. 42. 1160 g. 43. 87.6 kg. 44. 5.37 kg. 45. 946 kg. 46. 80.5%. 47. 11.73 tons. 48. 49 kg. 49. 3.67 kg. 50. 106.5 g. 52. 29.81%.

Sec. 4.1

23. 40%. 24. 50% H_2O, 16.7% CO_2, 33.3% O_2. 25. 22.4% CO_2, 67.2% CO, 10.4% N_2. 26. 6 tons. 27. Possible. 28. 14.96 m^3. 29. 67.2 litres each of CO and H_2. 30. 212.8 m^3 of CO_2 and 955.5 m^3 of NH_4OH solution. 31. 6.9 g of K_2CO_3. 32. 29.4% N_2 and 70.6% CO_2. 33. 50 g. 40. 45.8%. 41. 20.7% HCOONa and 6% NaOH. 42. 1.96%, 0.19 M. 43. 405 g of $Ca(HCO_3)_2$. 44. 103 litres, 347.4 ml. 49. 15% CO, 85% CO_2, 43.44% Na_2CO_3. 50. 40% CO, 60% CO_2, 16 ml. 51. 100 ml each of CO and O_2, 0.5 g of Na_2CO_3. 52. 5 moles and 3.01×10^{24} molecules. 53. 0.1 mole, 2.8 g. 54. $CaCO_3$. 55. C_2H_2 and C_6H_6. 56. 11.2 litres of CO and 16.8 litres of CO_2. 57. 60% CO_2 and 40% O_2. 59. 90.9%. 60. 290 kg. 61. 448 litres. 62. 396 kg. 63. 30.14 g. 64. 83%. 65. 63.5%. 66. (a) 22.4 litres and (b) 44.8 litres. 67. 83.36% Na_2CO_3. 68. 8 g of $CaCO_3$ and 8.4 g of $MgCO_3$. 69. 21.2 g of Na_2CO_3 and 1.7 g of $NaHCO_3$. 70. 10 molecules. 71. 26.5 g. 72. 5 g. 73. 83%.

Sec. 4.2

16. 70% Si and 30% C, 11.2 litres of H_2. 17. 37.3 ml. 20. 1.9 ml. 21. 19 g, 94.2 ml. 22. 1.35 g of H_2O and 2.25 g of SiO_2. 23. Si_2H_6. 28. 22.2 kg, 20.9 kg, and 75.3 kg. 37. 18.9% $NaHCO_3$. 38. 1.12 litres, 3.1%, 0.8 M. 39. 0.896 litre of CO_2 and 4.6% $Ba(HCO_3)_2$. 40. 2.14 tons of SiO_2 and 0.91 ton of CaC_2. 41. 16.7 kg of SiO_2 and 9.18 kg of C. 42. 793, 226.2 and 232.4 kg of SiO_2, Na_2CO_3 and $CaCO_3$, respectively. 43. 80%. 44. 46%. 45. 73, 18 and 29 kg of SiO_2, $CaCO_3$ and Na_2CO_3, respectively. 46. 222, 209 and 750 kg of Na_2CO_3, $CaCO_3$ and SiO_2, respectively. 47. 21 g of silicon and 1656 ml of NaOH solution. 48. 19.5 g.

Sec. 5.1

27. Its weight will become 5.08 g. 28. 50.5% Cu and 49.5% Al. 29. 20 g. 30. 96 g. 31. 56% iron and 44% copper. 32. 23.3 ml. 33. 32.5% zinc and 67.5% aluminium. 34. Mercury. 35. 93.3%, 500 ml. 36. 29.1%. 37. 6.6 ml. 38. 48.8 g of Cu and 156 g of acid. 39. 0.02 mole of Fe, 0.01 mole of Cu, 0.04 mole of O_2. 41. 63.2% Cu, 36.8% Fe, 27.7 ml of HNO_3. 42. 54% Al, 24% Mg, 22% Cu, 48.8 ml of NaOH solution. 43. 4.3% Al, 67.4% Fe, and 28.3% Cu. 44. 75% Al, 8.3% Fe, 16.7% Cu. 45. 11.9 g of Sn and 20.7 g of Pb. 46. 540.4 ml.

Sec. 5.2

20. 2.7%. 21. $Na_2S_2O_4$. 22. 15.6 g of potassium and 22.4 g of KOH. 23. Potassium. 27. 2.55 litres. 29. 6 g. 30. 62.9% H_2O, $Na_2CO_3 \times$ $\times 10H_2O$. 31. 79% NaOH, 21% Na_2CO_3, 2.24 litres of CO_2. 32. 275.5 ml. 33. 16.7% NaOH, 268 litres of CO_2, 20.2% Na_2CO_3. 34. 4.2 g of $NaHCO_3$, 2.65 g of Na_2CO_3, 1.68 litres of CO_2. 35. 53% $Na_2SO_4 \cdot 10H_2O$, 47% $Na_2CO_3 \cdot 10H_2O$, 2.68 ml of acid. 36. 37% $CaCO_3$, 63% $Ca(HCO_3)_2$, 19.2 ml of alkali. 37. 2.1 g of Na_2CO_3 and 0.82 g of NaOH. 38. 78% $KHCO_3$ and 22% KOH. 39. 143 g of $Na_2CO_3 \cdot 10H_2O$ and 357 g of H_2O. 40. 56%. 41. 4.6 g. 42. 126 g of $NaHCO_3$. 43. 6.04 g of KNO_3 and 8.52 g of $NaNO_3$. 44. 0.38 g of NaCl and 1.36 g of KCl.

Sec. 5.3

32. 4.45 litres. 33. 112 kg. 34. 28 g of CaO and 9 g of H_2O. 35. 202.5 g. 36. 3.7 g. 39. 12.7 milliequivalents/litre. 41. 230.55 g. 42. 64% $CaCO_3$, 36% CaO, 113.6 ml of acid. 43. 3.3%, 120 ml. 44. 1 g of $CaCO_3$ and 0.73 g of $SrCO_3$. 45. 1 : 1. 46. 3.57 g. 47. 80% $CaCO_3$ and 20% $Ca(OH)_2$. 48. 15.32 g. 49. 60.54 litres. 51. 253 g. 52. 5 milliequivalents/litre. 54. 12 g of $CaCO_3$ and 12.6 g of $MgCO_3$. 55. 1.14 g.

Sec. 5.4

18. 5.2 kg. 20. 2.7 g. 21. 1305 kJ. 26. 37% Cu and 63% Al. 27. 30.24 ml. 28. 68% Al and 32% Cu. 30. 13.3% 39.6 litres of H_2. 31. 27.3% Al and 72.7% Mg. 32. 70% Cu and 30% Al. 33. 10 ml, 10.8 g. 34. 24.3% Al, 75.7% Fe, 22 ml of acid. 35. Al and Cu. 36. 1.08 g of Al. 37. 0.05 mole/litre. 38. 17.3% $KHCO_3$, 54 g of Al. 39. 1.92 g of Cu and 1.08 g of Al. 40. 5.4 g. 41. 3 : 4. 42. 100.8 litres. 43. 27 g of Al. 44. 144 g. 45. 30 litres. 46. 83.3%. 47. 18% Al, 82% Fe, 23.25 ml of NaOH. 48. 5.36%. 49. 10.33 g. 50. 13.35 g.

Sec. 5.5

14. 28.1 ml. 15. 4.14 *M*. 18. 15 g and 2.24 litres. 19. 4.95 g. 21. 78 g of Cr and 40.5 g of Al. 36. 1435.9 kg. 38. $CrCl_3 \cdot 6H_2O$. 39. 6.72 litres.

Sec. 5.6

15. 33 g, 166.6 kJ. 17. 4.48 litres, 17.8 g. 24. 17.9 g, 3.7% KOH, 47.6% KNO_3, 40% KNO_2.

Sec. 5.7

25. 45.4 tons. 26. 28. 27. 1.89 kg. 29. 48.23 g. 30. 10 ml. 31. 73.7% Fe, 34.6 ml. 38. 62.2% Fe, 30% Al, 7.8% Cu. 39. 93.3% Fe, 36.7 ml of acid. 40. 38.1 g, 199.5 ml. 41. 5.6 g of Fe and 7.2 g of FeO. 42. 50 ml, 17.4% $NaHCO_3$. 43. 0.4 g. 44. 28% Fe, 36% FeO, 36% Fe_2O_3. 45. 104.4 ml of solution and 4.81 litres of Cl_2. 46. 12.8 g, 3.5 ml. 47. 112 g. 48. 0.672 litre. 49. 20.7 kg. 50. 1.6 g, 3.31 ml. 51. 21.6 g of FeO and 5.6 g of Fe. 52. 0.366 g of $FeSO_4$ and 0.836 g of $CuSO_4$. 53. 10 ml. 54. 4 ml. 55. 1.62 g.

Sec. 6.1

25. (a) 33.6 litres and (b) 1.12 litres. 28. C_3H_8. 29. C_3H_6. 30. C_6H_{14}. 32. (a) 16 g, (b) 0.2 mole and (c) 20 litres. 33. 30 m^3. 34. 10.7 kg. 35. 4.1 m^3. 36. C_3H_7Cl. 37. 10 litres. 38. 39.5 m^3. 39. 3.214 g. 40. 58 and 2. 41. C_5H_{12}. 43. C_3H_8. 45. 693.2 g. 46. C_4H_{10}. 47. C_2H_6. 49. 35.71 g and 107.14 g.

Sec. 6.2

21. Nearly 0.21 mole of C_2H_4 and 0.16 mole of C_3H_6. 22. (a) 147 g and (b) 196 g. 23. 8 g each. 24. 6.6 litres. 25. 22.4% C_2H_4 and 77.6% C_2H_6. 28. 3.925 g. 29. 800 m^3. 30. 328.9 litres. 34. 32 kg. 35. 80%. 36. 6.85 g and 2.24 litres. 37. 16.9%. 38. 88.4 g. 39. 34.5 m^3. 40. 55.8 g, 33.3% C_2H_2. 41. 18 litres and 10 litres. 42. 666.6 litres. 43. 66.66% CH_4 and 33.34% C_2H_2. 44. 66.66% C_3H_6 and 33.34% C_2H_2. 45. 14 litres and 160 g. 46. 28 litres of O_2 and 140 litres of air. 47. 89.6 litres and 240 g. 48. 100.8 litres. 49. 1 : 1. 51. 33.6 litres. 52. 224 litres and 495 g. 54. 8 g. 55. C_3H_6. 56. 4.48 litres.

Sec. 6.3

15. 13.4 litres. 16. 3.48 kg. 17. 18.4 g. 19. 9.44 ml. 20. 554.6 g. 21. 80.5 kg. 22. 17.2 m^3. 23. 58.2 g. 24. 234 g. 26. 168 litres. 27. 235.5 g. 28. 896 litres. 29. 95.54%. 30. 201.6 litres. 31. 2.65 g. 32. 56 g. 34. 168.7 g of C_6H_{12} and 227.13 m^3 of Cl_2.

Sec. 7.1

29. 1.71 tons. 30. 5.6 kg. 31. 69.12% C_2H_5ONa, 22.74% C_2H_5OH and 8.14% NaOH. 32. 74.8 litres and 176 ml. 33. C_4H_9OH. 34. C_3H_7OH. 35. 77.5 g. 36. 64.95 g. 37. 280 litres of air and 35.2 litres of CO_2. 38. 37% C_2H_5OH and 13% CH_3OH. 39. 73.6% CH_3OH and 26.4% C_2H_5OH. 40. 28.7 ml. 41. 310 kg, 12% excess ethylene oxide. 42. 9.3 g. 43. 1.12 litres. 44. (a) 50% and (b) 22.4%. 45. 16.3 ml. 49. 7.12 kg, 4.58 litres. 50. 5.6 g. 51. 59.18% C_6H_5ONa.

52. 44% phenol. 53. 1.4 g. 54. 19.85 ml. 55. 67.15% C_6H_5OH and 32.85% C_2H_5OH. 56. 1200 g. 57. 1.68 litres. 58. 5.18%. 59. 19.04 litres. 60. C_2H_6O. 61. CH_3OH. 63. 28 g.

Sec. 7.2

20. 20%. 21. 5.6 m^3. 22. 204.5 ml. 24. $C_5H_{10}O$. 25. 0.7 ml. 29. 72 g. 30. 40.54% HCOH and 59.46% CH_3COH. 31. 88%.

Sec. 7.3

22. $C_6H_{12}O_2$. 23. 154.1 ml. 24. 29.9 litres. 26. 20% acid and 31.3% phenol. 27. 9.5 ml. 29. 7.32 g. 30. 350 g. 31. 23 g each of acid and alcohol. 32. 7.46 litres. 33. 13.3 g. 34. 10.8 g of HCOOH and 24 g of $NaHSO_4$. 35. 48.3 g. 38. Linoleic acid. 40. 25.6 kg. 41. 12.2 ml. 42. C_2H_5OH. 43. 25% CH_3COOH and 75% HCOOH. 44. 7.36%. 45. 7.46 litres. 46. 305.8 ml. 47. 3400 kg. 48. 2.3 g.

Sec. 7.4

16. 27 g. 18. 9.1 ml of C_3H_7OH and 6.4 ml of C_2H_5OH. 19. $CH_3COOC_2H_5$. 20. $HCOOC_2H_5$. 21. 48% $CH_3COOC_2H_5$ and 52% CH_3COOCH_3. 22. 58.5% CH_3COOH and 41.5% HCOOH. 23. 70.4% $CH_3COOC_2H_5$ and 29.6% $HCOOC_2H_5$. 24. $HCOOCH_3$. 25. 67.3 g of acid and 29.1 g of alcohol. 28. 30.2 kg. 29. 88.4 g. 30. 25 ml. 31. 15.2 m^3. 32. 23.26 g. 33. 90 g. 35. 2.64 g of $CH_3COOC_2H_5$ and 2.96 g of $HCOOC_2H_5$. 38. 34.78 g.

Sec. 7.5

15. 89.6 litres. 16. 268.8 litres. 17. 121.8 g. 18. 24.5 litres. 21. 49.2% glucose, 25.7% phenol and 25.1% glycerol. 22. 4.48 litres, 36.4 g. 23. 2250 litres. 24. 9.5 tons. 28. $n = 10802$; 35.9 ml of acid.

Sec. 8.1

20. 1.55 g. 23. 9.3 g. 24. 35.1% aniline, 35.5% phenol and 29.4% benzene. 25. 12.2 ml. 26. 4.6 g of C_2H_5OH, 12 g of C_3H_7OH and 66.4 g of mixture.

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